

PB90-151770

Exposure to Chemical Additives from Polyvinyl
Chloride Polymer Extrusion Processing

Southwest Research Inst., San Antonio, TX

Prepared for:

Environmental Protection Agency, Cincinnati, OH

Dec 89



U.S. Department of Commerce
National Technical Information Service

NTIS

TECHNICAL REPORT DATA		
(Please read Instructions on the reverse before completing)		
1. REPORT NO. EPA/600/2-89/063	2.	3. RECIPIENT'S ACCESSION NO. 190 151770/AS
4. TITLE AND SUBTITLE Exposure to Chemical Additives from Polyvinyl Chloride Polymer Extrusion Processing		5. REPORT DATE December 1989
7. AUTHOR(S) Cathy S. Lamb		6. PERFORMING ORGANIZATION CODE
9. PERFORMING ORGANIZATION NAME AND ADDRESS Southwest Research Institute 6220 Culebra Rd. San Antonio, TX 78284		8. PERFORMING ORGANIZATION REPORT NO.
12. SPONSORING AGENCY NAME AND ADDRESS Risk Reduction Engineering Laboratory Office of Research and Development U.S. Environmental Protection Agency Cincinnati, OH 45268		10. PROGRAM ELEMENT NO.
		11. CONTRACT/GRANT NO. CR813355
		13. TYPE OF REPORT AND PERIOD COVERED Project Report
15. SUPPLEMENTARY NOTES Project Officer - Dennis L. Timberlake		14. SPONSORING AGENCY CODE EPA/600/14
16. ABSTRACT This report presents a model to predict worker inhalation exposure due to off-gassing of additives during polyvinyl chloride (PVC) extrusion processing. Data on off-gassing of additives were reviewed in the literature, the off-gassing at normal PVC processing temperatures was studied in the laboratory, process variables were estimated from an equipment manufacturer survey, and worker activities and possible exposure sources were observed in an industrial survey. The purpose of this study was to develop a theoretical model to predict worker inhalation exposure to additives used during PVC extrusion processing. A model to estimate the generation rate of the additive from the polymer extrudate was derived from the mass transport equations governing diffusion. The mass flow rate, initial additive volatile weight fraction, off-gassing time, diffusivity, and slab thickness are required to determine the generation rate from the model.		
17. KEY WORDS AND DOCUMENT ANALYSIS		
a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
18. DISTRIBUTION STATEMENT Release to Public	19. SECURITY CLASS (This Report) Unclassified	21. NO. OF PAGES
	20. SECURITY CLASS (This page) Unclassified	22. PRICE

EPA/600/2-89/063
December 1989

EXPOSURE TO CHEMICAL ADDITIVES FROM
POLYVINYL CHLORIDE POLYMER EXTRUSION PROCESSING

by

Cathy S. Lamb
Southwest Research Institute
San Antonio, Texas 78228-0510

EPA Cooperative Agreement CR813355

Project Officer

Dennis L. Timberlake
Water and Hazardous Waste Treatment Research Division
Risk Reduction Engineering Laboratory
Cincinnati, Ohio 45268

RISK REDUCTION ENGINEERING LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
CINCINNATI, OHIO 45268

DISCLAIMER

The information in this document has been funded wholly or in part by the United States Environmental Protection Agency under Cooperative Agreement CR813355 with Southwest Research Institute. It has been subjected to the Agency's peer and administrative review, and it has been approved for publication as an EPA document. The use of trade names or commercial products does not constitute endorsement or recommendation by the United States Environmental Protection Agency.

FOREWORD

Today's rapidly developing and changing technologies and industrial products and practices frequently carry with them the increased generation of materials that, if improperly dealt with, can threaten both public health and the environment. The U.S. Environmental Protection Agency is charged by Congress with protecting the Nation's land, air, and water resources. Under a mandate of national environmental laws, the agency strives to formulate and implement actions leading to a compatible balance between human activities and the ability of natural systems to support and nurture life. These laws direct the EPA to perform research to define our environmental problems, measure the impacts, and search for solutions.

The Risk Reduction Engineering Laboratory is responsible for planning, implementing, and managing research, development, and demonstration programs to provide an authoritative, defensible engineering basis in support of the policies, programs, and regulations of the EPA with respect to drinking water, wastewater, pesticides, toxic substances, solid and hazardous wastes, and Superfund-related activities. This publication is one of the products of that research and provides a vital communication link between the researcher and the user community.

This report presents a model to predict worker inhalation exposure due to off-gassing of additives during polyvinyl chloride (PVC) extrusion processing. Data on off-gassing of additives were reviewed in the literature, the off-gassing at normal PVC processing temperatures was studied in the laboratory, process variables were estimated from an equipment manufacturer survey, and worker activities and possible exposure sources were observed in an industrial survey.

E. Timothy Oppelt, Director
Risk Reduction Engineering Laboratory

ABSTRACT

This report presents a model to predict inhalation worker exposure due to off-gassing of additives during polyvinyl chloride extrusion processing. Existing literature was reviewed to obtain data on off-gassing of additives in polymer processing operations. To supplement the information obtained in the literature survey, the off-gassing of additives at normal polyvinyl chloride processing temperatures was studied in the laboratory using gas chromatography/mass spectroscopy analysis to identify the off-gassed compounds. Estimations of the process variables necessary to evaluate the generation rate from the model were collected in an equipment manufacturer survey. The industrial data survey was conducted to observe worker activities and possible exposure sources under normal processing conditions.

The purpose of this study was to develop a theoretical model to predict inhalation worker exposure during polyvinyl chloride extrusion processing. A model to estimate the generation rate of the additive from the polymer extrudate was derived from the mass transport equations governing diffusion. The mass flow rate, initial additive volatile weight fraction, off-gassing time, diffusivity, and slab thickness are required to determine the generation rate from the model. Equations to estimate the initial volatile weight fraction of the additive and diffusivity based on the chemical properties of the additive and extrusion processing variables are included. The mass flow rate and off-gassing time for different applications and formulations are presented in tabular form. A Gaussian plume dispersion model was used to estimate the worker exposure from the generation rate data.

This report is submitted in partial fulfillment of Cooperative Agreement CR813355 by Southwest Research Institute under the partial sponsorship of the U.S. Environmental Protection Agency. This report covers a period from August 1, 1986 to May 10, 1988, and work was completed as of April 1, 1988.

CONTENTS

Foreword	iii
Abstract	iv
Figures	vii
Tables	viii
Abbreviations and Symbols	x
Acknowledgments	xiii
 1. Introduction	 1
2. Conclusions	4
3. Recommendations	6
4. Literature Survey	7
General	7
Phthalate plasticizer exposure	7
Lead exposure	10
VCM exposure	10
Summary	11
5. Laboratory Data Study	12
General	12
Differential scanning calorimetry	13
Pyrolysis literature review	13
Pyrolysis of polyvinyl chloride	14
Pyrolysis of PVC with additives	14
Pyrolysis study	20
Experimental equipment and conditions	20
Quality assurance plan	20
Experimental results	21
Discussion of results	24
Quality assurance results	25
Summary	26
6. Equipment Manufacturer Survey	27
General	27
Flexible and rigid formulations	27
Applications	29
Extrusion processing variables	29
Other processing techniques	29
Equipment configuration	30
Extruder	30
Cooling system	31
Collection device	32
Winder and cutting device	32
Summary	32
7. Industrial Data Survey	34
Plant A	34

CONTENTS (CONT'D)

High-speed mixer.	34
Pelletizer.	35
Wire coater	35
Sheet extruder.	35
Pipe extruder	36
Injection molding	36
Blow molding.	36
Plant B.	36
Plant C.	37
Summary.	37
8. Worker Exposure Model	39
Generation rate model.	39
Assumptions	40
Series summation.	42
Estimation of variables.	43
Volatile weight fraction.	43
Mass flow rate.	45
Off-gassing time.	45
Diffusivity	46
Concentration dependence	46
Temperature dependence	47
Molecular volume dependence.	48
Examples of generation rate calculations	50
Example 1. Diheptyl phthalate.	50
Example 2. Vinyl chloride monomer.	52
Worker exposure model.	54
Example 1. Diheptyl phthalate.	55
Example 2. Vinyl chloride monomer.	56
Model validation	56
References	58
Bibliography	62
Appendices	
A. Review of polymer processing techniques	63
B. Differential scanning calorimetry (DSC) plots of the various PVC commercial samples	67
C. Quality assurance project plan.	72
D. GC/MS identifications of off-gassed products at 300°C and 600°C.	92
E. LOTUS spreadsheet calculations.	102

FIGURES

<u>Number</u>		<u>Page</u>
A-1	Inverted L-shape.	64
B-1	DSC trace for sample PPR-T2-1, in air at 10°C/min .	67
B-2	DSC trace for sample PPR-T2-2, in air at 10°C/min .	68
B-3	DSC trace for sample PPR-T2-3, in air at 10°C/min .	69
B-4	DSC trace for sample PPR-T2-6, in air at 10°C/min .	70
B-5	DSC trace for sample PPR-T2-7, in air at 10°C/min .	71

TABLES

<u>Number</u>		<u>Page</u>
1	Summary of Literature Data on Worker Exposure From PVC Processing.	8
2	PVC Samples For Analysis.	12
3	Summary of Literature Data on Pyrolysis of Polyvinyl Chloride	15
4	Summary of Literature Data on Additive Effects on Pyrolysis of PVC	17
5	Average Weight Loss of PVC Samples After Pyrolysis.	21
6	Summary of Off-Gassed Products at 300°C, Helium Atmosphere.	22
7	Summary of Off-Gassed Products at 600°C, Helium Atmosphere.	23
8	PVC Additives	28
9	Values of $G/w_{AOM'}$ For Various D_{Atf}/L^2 Values.	42
10	Extrusion Mass Flow Rate Data	45
11	Off-gassing Time.	46
12	Atomic Volumes For Calculating Complex Molecular Volumes For Simple Substances.	49
13	Correction Factors For Ring Structures.	49
14	Values of Diffusivity in Polyvinyl Chloride at 35°C.	50
15	Diffusion Function, $1/(2\pi\sigma_y\sigma_z)$	55

TABLES (CONT'D)

<u>Number</u>		<u>Page</u>
D-1	Off-Gassed Products of Sample PPR-T2-1 at 300°C . .	92
D-2	Off-Gassed Products of Sample PPR-T2-2 at 300°C . .	93
D-3	Off-Gassed Products of Sample PPR-T2-3 at 300°C . .	94
D-4	Off-Gassed Products of Sample PPR-T2-6 at 300°C . .	95
D-5	Off-Gassed Products of Sample PPR-T2-7 at 300°C . .	96
D-6	Off-Gassed Products of Sample PPR-T2-1 at 600°C . .	97
D-7	Off-Gassed Products of Sample PPR-T2-2 at 600°C . .	98
D-8	Off-Gassed Products of Sample PPR-T2-3 at 600°C . .	99
D-9	Off-Gassed Products of Sample PPR-T2-6 at 600°C . .	100
D-10	Off-Gassed Products of Sample PPR-T2-7 at 600°C . .	101

ABBREVIATIONS AND SYMBOLS

ABBREVIATIONS

Å	-- angstrom
BuBzP	-- butyl benzyl phthalate
°C	-- degrees Celsius
cal	-- calorie
CDS	-- Chemical Data System, Inc.
CI	-- chemical ionization
cm	-- centimeter
CORR	-- correction
DBP	-- dibutyl phthalate
DC	-- direct current
DCP	-- o-dicapryl phthalate
DDP	-- diisodecyl phthalate
DEHP	-- di(2-ethylhexyl) phthalate
DHP	-- diheptyl phthalate
DHXP	-- dihexyl phthalate
DOP	-- di(2-ethylhexyl) phthalate
DSC	-- differential scanning calorimetry
EPA	-- U.S. Environmental Protection Agency
ft	-- foot
g	-- gram
GC	-- gas chromatography
HPLC	-- high performance liquid chromatography
hr	-- hour
ID	-- identification
IR	-- infrared spectrometry
kcal	-- kilocalorie
kg	-- kilogram
m	-- meter
mg	-- milligram
min	-- minute
mL	-- milliliter
mm	-- millimeter
MS	-- mass spectrometry
ND	-- not detected
ng	-- nanogram
NTIS	-- National Technical Information Service
PAH	-- polycyclic aromatic hydrocarbon
PMMA	-- poly(methyl methacrylate)
PMN	-- Premanufacture Notice
PMR	-- Proton magnetic resonance
ppm	-- parts per million

ABBREVIATIONS AND SYMBOLS (CONT'D)

ABBREVIATIONS

psi	-- pounds per square inch
psig	-- pounds per square inch gauge
PVC	-- polyvinyl chloride
QA	-- quality assurance
Ref	-- reference
s	-- second
SwRI	-- Southwest Research Institute
TSCA	-- Toxic Substances Control Act
TWA	-- time weighted average
μ g	-- microgram
U.S.	-- United States
VCM	-- vinyl chloride monomer
wt.	-- weight

SYMBOLS

$\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$	-- alumina trihydrate
Ar	-- argon
CaCO_3	-- calcium carbonate
Cd	-- cadmium
CdCl_2	-- cadmium chloride
CH_4	-- methane
C'_{max}	-- concentration of additive in ppm(v)
CO	-- carbon monoxide
CO_2	-- carbon dioxide
CuC_2O_4	-- copper oxalate
D_A	-- additive mass diffusivity
D_{AO}	-- diffusivity constant
d_{max}	-- maximum valid distance
E_D	-- activation energy
G	-- generation rate
h	-- height of source above floor
HCl	-- hydrochloric acid
L	-- thickness of slab
m'	-- mass flow rate
M	-- molecular weight
N_2	-- nitrogen
NaOH	-- sodium hydroxide
P	-- pressure, atm
P°	-- vapor pressure, atm
$\text{Pb}_2(\text{SO}_4)_3$	-- lead sulfate
Q	-- amount of chemical generated per unit area
R	-- gas law constant
Sb_2O_3	-- antimony trioxide
Sb_2O_5	-- antimony oxide
SbCl_3	-- antimony chloride

ABBREVIATIONS AND SYMBOLS (CONT'D)

SYMBOLS

T	-- absolute temperature
t	-- time
t _f	-- off-gassing time
U	-- velocity of ambient air in ft/min
V	-- volumetric flow rate
V _A	-- molal volume of additive at normal boiling point
w _{AO}	-- initial volatile weight fraction
x _{AO}	-- initial volatile mole fraction
Z	-- direction perpendicular to flat surface
ΔH	-- heat of vaporization
ρ _A	-- additive mass concentration
ρ _{AO}	-- initial additive mass concentration
μ _B	-- viscosity of solution
Φ _B	-- association parameter for solvent B
σ _Y σ _Z	-- diffusion coefficients

ACKNOWLEDGMENTS

Many people have contributed to the preparation of this document. The author would like to acknowledge the efforts of these individuals for their contributions. The differential scanning calorimetry data was provided by Mrs. Karen Kohl and Ms. Virginia Barnhill. The pyrolysis/gas chromatography/mass spectrometry data were provided by Mrs. Patricia Kuhrt and Ms. Ellen Leng. The first part of the study, including the literature survey, laboratory data study, and industrial data study, was conducted under the direction of Dr. David Trujillo. His initial work and assistance on the remainder of the project is greatly appreciated. The review of this document by Mrs. Mary Marshall, and Dr. David Trujillo assisted in the final preparation of this report. The work of Mrs. Sharon McFaddin in typing the manuscript is greatly appreciated.

SECTION 1

INTRODUCTION

Under section 5 of the Toxic Substances Control Act (TSCA), industry must notify the U.S. Environmental Protection Agency (EPA) of its intent to manufacture, process, or use a chemical substance that is not included on the TSCA chemical substance inventory. The company must submit a Premanufacture Notice (PMN) at least ninety days before the commercialization of a new chemical substance or employment of a "significant new use" of an existing chemical. During this review period, EPA assesses the risk of the new chemical to human health and the environment. As a result of this investigation, EPA may require testing, issue a limitation or ban, or regulate the production or use of the chemical substance if the chemical poses an unreasonable risk to human health or the environment.

Review of polymer additives under the PMN system has raised concerns about potential worker exposure. During polymer processing operations, the polymer, blended with additives, is heated and shaped into the final product. This heat treatment could cause off-gassing of residual monomer, polymer degradation products, polymer additives, and polymer additive degradation products into the worker environment. To evaluate the risk to human health and the environment, EPA must estimate the potential worker exposure and chemical release involved in different polymer processing operations. EPA currently possesses only limited information on worker exposure levels and controls used to minimize exposure in polymer processing.

Under a cooperative agreement with the EPA, Southwest Research Institute (SwRI) conducted a polymer processing research study to develop a model to evaluate inhalation worker exposure to additives used in polyvinyl chloride (PVC) extrusion processing. This study focused on extrusion processing because most thermoplastics are extruded in either the compounding or fabrication stage. In compounding, the extruder melts the polymer, blends the additives into the melt, and forms pellets of blended polymer, which can be used as the starting material in other processes, such as injection molding or blow molding. In fabrication, pellets are extruded to form a finished product, such as pipe, tubing, or profiles. A review of extrusion and other polymer processing techniques is included in Appendix A. Polyvinyl chloride, the third largest volume extrusion resin, was

selected for this study because PVC contains more types and amounts of additives than the two larger volume systems. The extrusion temperature for polyvinyl chloride ranges from 150°C to 210°C, which may cause off-gassing of some chemical additives. The primary objective of this study was to develop a model to predict the amount of a new chemical additive off-gassing into the workers' environment. Before developing this model, the important variables affecting off-gassing were determined from a literature survey, a laboratory data study, an equipment manufacturer survey, and an industrial data survey.

A literature review was conducted to obtain existing data on off-gassing of additives in PVC extrusion. The purpose of the survey was to determine whether any worker exposure data existed which had been correlated to types of additives, extrusion process variables, and worker activities. The available literature on worker exposure was also evaluated to determine the important variables that affect off-gassing, such as temperature, additive vapor pressure, and throughput rates.

To supplement the information obtained in the literature survey, the off-gassing of additives at normal PVC processing temperatures was studied in the laboratory using gas chromatography/mass spectrometry (GC/MS) analysis to identify toxic compounds. Commercial samples of polyvinyl chloride, with and without additives, were pyrolyzed, and the off-gassed compounds were identified by GC/MS. The purpose of the study was to determine whether off-gassed compounds could be correlated to specific additives and to study the effect of temperature on the amount and type of materials off-gassed.

The equipment manufacturer survey was conducted to obtain information on process variables that affect off-gassing of additives. The purpose of the survey was to determine and estimate process variables necessary to evaluate the generation rate from the theoretical model, such as maximum throughput. The dependence of different cooling systems and the off-gassing time upon types of extruded products was also investigated.

The industrial data survey was conducted to observe worker activities and to identify possible exposure sources under normal processing conditions. Walk-through surveys at polymer processing plants were conducted to obtain information on worker activities, possible exposure sources, ventilation controls, and cooling systems. The dependence of these variables on the type of process and final product was also examined.

Because the PMN system supplies only limited processing information relative to the additives, a reasonable worst case model for the generation rate of chemical additives was derived using several simplifying assumptions. A model to estimate the worker exposure from the generation rate based on air turnover or

7

ventilation rates was developed using a Gaussian plume dispersion model. Estimations of key variables, such as volatile mass fraction, mass flow rate, diffusivity, and off-gassing time were included to evaluate the model in the limited time frame available under the PMN system.

SECTION 2

CONCLUSIONS

The literature survey did not provide sufficient information on inhalation worker exposure due to off-gassing of additives during PVC extrusion. The articles on phthalate plasticizer exposure involved a different type of processing, calendering. The exposure mechanism for lead stabilizers is generation of dust not off-gassing of volatiles. Although information on exposure to vinyl chloride monomer is more extensive, the literature did not provide sufficient information on process variables, such as initial concentration, temperature, ventilation rates, and off-gassing time.

Although the literature search lacked information on operating parameters, some important variables were identified. These variables include PVC film thickness, additive vapor pressure, and exhaust ventilation. The dependence of worker exposure on film thickness indicates a diffusion-controlled mechanism for off-gassing. An additive with a lower vapor pressure has a lower generation rate. Local exhaust ventilation for calendering and compounding operations reduced the worker exposure level.

The laboratory data study shows that little or no off-gassing occurred at the normal processing temperature of 150°C. As the temperature is increased to 300°C, off-gassing results in significant weight losses for the polyvinyl chloride samples. Most of this weight loss is associated with the degradation of the polyvinyl chloride, although some off-gassed compounds were attributed to additives. The potential for each additive to off-gas depends on its chemical structure and properties, including physical state at the pyrolysis temperature and diffusivity in polyvinyl chloride.

The major source of exposure to off-gassed additives is the hot extrudate leaving the extruder die. Depending on the cooling method utilized, the exposure source would be either a short segment of the extrudate between the extruder and a water trough or vacuum former, or a longer portion if air cooling is used.

The off-gassing time depends primarily on the cooling method which depends on the type of compound and end product. The longest off-gassing times would occur for rigid compounds which are air cooled. The off-gassing time would be the time required for the extrudate to cool below the glass transition temperature. The off-gassing time for the other cooling methods is the time necessary for the extrudate to travel between the extruder and the water trough or vacuum former.

From the walk-through surveys, there were no evident sources of exposure in injection molding, blow molding, and compression molding, because the units were completely enclosed. The finished product is not exposed to the workplace environment until the product is cooled.

The model developed from transport equations predicts reasonable worst case estimates based on generalized comparisons with the limited data presented in the literature. The lack of information in the literature necessitated making assumptions to estimate the exposure from the model, thus the literature data cannot be used to validate the model.

SECTION 3

RECOMMENDATIONS

The model should be validated using worker exposure measurements taken at industrial processing plants or in pilot plant studies with laboratory extruders. This data should include measurements of the model variables, so the effectiveness of the estimation techniques can be evaluated.

The model should be extended to include different polymers and processing techniques. To extend the model to different polymers, information on the difference in processing techniques and physical properties would have to be collected. This information would include the quantity and type of additives commonly used, processing temperatures, cooling systems, mass flow rates, off-gassing time, and the diffusional properties of the polymers. Polymers, such as fluoroplastics, polysulfones, polyether ether ketone, polyesters, polyetherimide, and polyphenylene sulfide, should be considered for further investigation because of the higher processing temperatures. To extend the model to different polymer processes would require collecting information on exposure sources, off-gassing time, and processing variables, such as temperature and flow rates.

SECTION 4

LITERATURE SURVEY

GENERAL

The literature survey was conducted to obtain existing information on worker exposure to off-gassed compounds during PVC extrusion processing. The purpose of the study was to correlate the worker exposure to types of additives, worker activities, and other processing variables. The literature search aided in identifying variables that affect the worker exposure to off-gassed compounds.

A search of computer data bases for literature on worker exposure to polyvinyl chloride produced twenty relevant articles. The computer data bases searched included: Chemical Abstracts, Biosis Previews, Compendex, Environmental Bibliography, Enviroline, Medline, and NTIS. A preliminary search revealed 173 unique literature citations; twenty of these articles were obtained and examined carefully. The articles not reviewed contained information on medical effects attributed to exposure to PVC, but neglected information on exposure levels or worker activities. Of the twenty articles reviewed, eleven dealt exclusively with exposure to vinyl chloride monomer (VCM) in the production of polyvinyl chloride. The remaining nine articles documented worker exposure to phthalate plasticizers, lead stabilizers, or vinyl chloride monomer in the processing of polyvinyl chloride. Table 1 presents a summary matrix of the chemical exposure material, worker activities, the inhalation exposure level, and air monitoring method.

PHthalate PLASTICIZER EXPOSURE

Three articles reported the worker exposure levels for phthalate plasticizers during PVC processing. In 1969, a study in the Soviet Union reported values of 1.7-66 mg/m³ of the plasticizer, dibutyl phthalate (DBP), in the working zones of primers, calender operators, and mixers.¹ The phthalate plasticizer was the principal component of the gaseous environment, but the levels of vinyl chloride, carbon monoxide, and hydrogen chloride were also monitored. The two more recent studies have shown concentrations below the threshold limit value of 5 mg/m³. The second study reported values of 0.06 - 0.29 mg/m³ of di-(2-ethylhexyl) phthalate at a PVC sheet processing

TABLE 1. SUMMARY OF LITERATURE DATA ON WORKER EXPOSURE FROM PVC PROCESSING

Ref	Chemical exposure material	Worker activities (# of workers)	Chemical exposure TWA	Air monitoring method
1	Phthalate plasticizer	Primers (60) Calender and mill operators (28) Mixing operators and paint millers (35)	10-66 mg/m ³ 10-66 mg/m ³ 1.7-40 mg/m ³	Not specified
2	Di-2-(ethyl hexyl)phthalate	Compounder Feed operator Calender utility man	0.06 mg/m ³ 0.29 mg/m ³ 0.09 mg/m ³	Millipore filters with DuPont P-2500 pumps
3	Phthalate plasticizer	Thin department Calender operators (5) Machine attendants (8) Repair men (1) Mixing workers (3) Thick department Calender/machine attendants (10)	2.0 mg/m ³ 0.2 mg/m ³ 0.3 mg/m ³ 0.02 mg/m ³ 0.4 mg/m ³	Glass fiber filters with MSA pump Type G
4	Lead stabilizers	Blenders of powdered stabilizers (14) Blenders of oil mixed stabilizers (10) Blenders of encapsulated stabilizers (10)	250.9 ug/m ³ 70.6 ug/m ³ 9.8 ug/m ³	Millipore filters with DuPont P-4000 pumps
5	Vinyl chloride monomer	Firm and mold plants Pipe and mold plants	3 ppm <1 ppm	Not specified
6	Vinyl chloride monomer	Area samples	0.45-1.3 ppm	Detector tubes
	HCl	Area samples	ND	
	CO	Area samples	ND	
	CO ₂	Area samples	ND	
	Phosgene	Area samples	ND	
	Chlorine	Area samples	ND	
7,8,9	Vinyl chloride monomer	Plant G Compounding (8) Extrusion (24) Laboratory (4)	<0.01 ppm <0.01 ppm <0.01 ppm	Charcoal tubes with Model SP-1 siphon pumps
7,8,9	Vinyl chloride monomer	Plant H Compounding (8) Extrusion (16) Laboratory (8) Maintenance (8) Molding (8)	0.09 ppm 0.01 ppm 0.03 ppm 0.01 ppm 0.01 ppm	Charcoal tubes with Model SP-1 siphon pumps
7,8,9	Vinyl chloride monomer	Plant I Laboratory (4) Plastisol (40)	ND 0.01 ppm	Charcoal tubes with Model SP-1 siphon pumps

CONTINUED....

TABLE 1. (CONT'D)

Chemical exposure Ref material	Worker activities (# of workers)	Chemical exposure TWA	Air monitoring method
7,8, Vinyl chloride 9 monomer	Plant J		
	Calendering (12)	ND	Charcoal tubes with Model SP-1 siphon pumps
	Compounding (12)	ND	
	Extrusion (8)	ND	
	Molding (8)	ND	
	Miscellaneous (4)	ND	
7,8, Vinyl chloride 9 monomer	Plant K		
	Calendering (6)	<0.01 ppm	Charcoal tubes with Model SP-1 siphon pumps
	Compounding (12)	0.01 ppm	
	Maintenance (2)	<0.01 ppm	
7,8, Vinyl chloride 9 monomer	Plant L		
	Calendering (8)	1.48 ppm	Charcoal tubes with Model SP-1 siphon pumps
	Compounding (16)	0.42 ppm	
	Extrusion (10)	0.27 ppm	
	Laboratory (2)	0.33 ppm	
7,8, Vinyl chloride 9 monomer	Plant M		
	Calendering (2)	0.02 ppm	Charcoal tubes with Model SP-1 siphon pumps
	Compounding (22)	0.01 ppm	

ND - Not detected

facility in the United States in 1982.² The highest worker exposure level of 0.29 mg/m³ was reported for a feed operator. Area samples of the plant indicated the highest level of 4.23 mg/m³ occurred next to an extruding/heating screen outlet conveyor. The third study examined the exposure level for two different departments of a PVC processing plant in Sweden in 1985: a thin film calendering process, and a thick film floor sheeting calendering process.³ The thin film process used a combination of plasticizers including diisodecyl phthalate (DDP), di(2-ethylhexyl) phthalate (DEHP), and butyl benzyl phthalate (BuBzP). The thick film process employed DEHP and aliphatic hydrocarbons as plasticizers. The exposure levels ranged from 0.02 - 2 mg/m³. The calender workers in the thin film department were exposed to the highest level. The lower thick film exposure level indicates a diffusion-controlled off-gassing. The significantly lower phthalate concentration compared with the first study was attributed to better ventilation (exhaust vents above the calenders) and lower material vapor pressures (DDP and DEHP as compared with DBP).

LEAD EXPOSURE

One article reported on worker exposure to lead at a cable manufacturing plant in the United States in 1982.⁴ The lead exposure for blenders, who weighed and mixed the lead stabilizer into the PVC, was recorded for three different types of stabilizer: powdered, oil-mixed, and encapsulated. The personal air sample concentrations were 250.9 µg/m³ for the powdered stabilizer, 70.6 µg/m³ for the oil-enriched stabilizer, and 9.8 µg/m³ for the encapsulated stabilizer. The encapsulated stabilizer significantly reduced the worker exposure to lead dust.

VCM EXPOSURE

Five citations reported the worker exposure to vinyl chloride monomer in PVC processing plants. The first article presented VCM concentrations in the workers' breathing zones in two different types of U.S. fabrication plants in 1975.⁵ In seven firm and mold plants, the mean concentration was 3 ppm. In two pipe and mold plants, the mean concentration was less than 1 ppm. In the second article, VCM exposure levels of 0.45 - 1.3 ppm were measured for a PVC extruder in 1982.⁶ These studies were initiated to investigate complaints of respiratory irritations, headaches, and nausea from 62 of 201 workers after exposure to vapors from an overheated extruder (362°C). The illnesses were believed to be caused by exposure to HCl and CO, which are PVC decomposition products. No detectable concentrations of HCl, CO, CO₂, phosgene, or chlorine were observed at normal operating conditions. The last three citations resulted from a study by the U.S. National Institute for Occupational Safety and Health on worker exposure to VCM in

production and processing of polyvinyl chloride in 1975. 7,8,9 Worker exposure levels were measured for calendering, compounding, extrusion, molding, and plastisol operations at seven polymer processing plants. Only one plant had a VCM concentration above 0.1 ppm. The site of this processing plant also included polyvinyl chloride polymerization reactors. During the study, a rupture disc on a reactor failed releasing vinyl chloride vapors which were pulled into the processing plant by the ventilation system. The first article also included measurements of worker exposure to VCM between April, 1975 and April, 1978.⁷ Of the fifteen plants studied only one plant had a detectable level of VCM.

SUMMARY

Although the literature search lacked information on operating parameters, some important variables, such as PVC film thickness and additive vapor pressure, were identified. The off-gassing rate seems to depend on film thickness, indicating a diffusion-controlled mechanism. A plasticizer additive with a lower vapor pressure seems to cause a lower generation rate. Calendering and compounding had slightly higher exposure levels than extrusion processing. Local exhaust ventilation for calenders and compounding blenders reduced the worker exposure levels to phthalate plasticizers. The exact effect of ventilation controls is unknown because of the simultaneous change in local exhaust systems and the use of lower vapor pressure plasticizers. The exposure levels for VCM decreased after 1975, because of more stringent restrictions on the amount of residual vinyl chloride monomer in the polyvinyl chloride. Exposure to dust from lead stabilizers in compounding has also decreased because of encapsulation of the stabilizer. The literature citations did not contain much information on how extrusion processing variables, such as temperature, pressure, and flow rate, affected the off-gassing of additives in polyvinyl chloride.

SECTION 5

LABORATORY DATA STUDY

GENERAL

The laboratory data study was conducted to determine whether any toxic gaseous compounds are off-gassed as a result of the presence of additives at normal PVC processing temperatures. The laboratory data study consisted of two different techniques: differential scanning calorimetry (DSC) and pyrolysis coupled with gas chromatography/mass spectrometry analysis of off-gassed compounds. The analyzed samples included an engineering resin, two different wire jacketing compounds, a pipe extrusion resin, and a window profile resin. Table 2 identifies the samples with an SwRI identification number and lists the general category of additives present.

TABLE 2. PVC SAMPLES FOR ANALYSIS

SwRI ID #	Comments	Additives
PPR-T2-1	Wire jacketing compound, white irregular pellets, flexible PVC.	Plasticizer (30%); Stabilizer (2%); Filler (19%)
PPR-T2-2	Wire jacketing compound, white irregular pellets, flexible PVC.	Plasticizer (31%); Stabilizer (2%); Filler (19%)
PPR-T2-3	Engineering resin, clear irregular pellets, rigid PVC.	Lubricant (2%); Stabilizer (2%)
PPR-T2-6	Pipe extrusion resin, white powder, rigid PVC.	Stabilizer; copolymer; filler; lubricant
PPR-T2-7	Window profile resin, white powder, rigid PVC.	Stabilizer; lubricant; filler; impact modifier; pigment

The samples were analyzed by DSC to determine the degradation temperature and the effect of gradually increasing the temperature. In the pyrolysis study, the samples were heated quickly to a predetermined temperature for a short time, and the gaseous byproducts were analyzed using GC/MS. Although pyrolysis does not exactly duplicate the extrusion process, pyrolysis for short periods of time at the extrusion temperature can be used to simulate the extrusion process. In extrusion, the polymer is heated by contact with the extruder wall and by mechanical shearing of the polymer. As the extrudate leaves the extruder, the extrudate surface cools resulting in a hardened shell and a molten core. The pyrolysis procedure duplicates the heating of the polymer by contact with a hot surface but does not account for the heat due to mechanical shearing. The pyrolysis sample is then cooled, and the gaseous products analyzed by GC/MS.

DIFFERENTIAL SCANNING CALORIMETRY

The samples were analyzed by differential scanning calorimetry to determine the temperature at which degradation of the sample begins. In DSC, the differential heat flow required to maintain a sample of the material and an inert reference at the same temperature is measured. A DuPont 9900 differential scanning calorimeter individually heated the sample and the reference in air at 1 atmosphere from 20°C to 300°C at a rate of 10°C/min. The DSC plots for the polyvinyl chloride samples are included in Appendix B. The first slight change in slope of the DSC trace was recorded between 180°C and 220°C. This endothermic deviation indicates the initiation of dehydrochlorination at weak points in the PVC chain.¹⁰ The endotherm gradually steepens indicating the random dehydrochlorination of polyvinyl chloride. For the two wire jacketing compounds, an exothermic peak was detected at 260°C to 270°C. This peak was attributed to the exothermic reaction of HCl with calcium carbonate or calcium hydroxide, which are commonly used as fillers. This peak was followed by the endotherm for random dehydrochlorination of polyvinyl chloride. For the pipe extrusion and window profile resin, the exothermic reaction of a smaller amount of filler is masked by the endothermic dehydrochlorination process.

PYROLYSIS LITERATURE REVIEW

Before initiating the pyrolysis study, a literature review on the pyrolysis of PVC was conducted. Ten articles about the pyrolysis of PVC without additives were reviewed to find the decomposition products of polyvinyl chloride, so the effect of additives could be determined. Nine articles on additive effects on pyrolysis products of PVC were also examined.

Pyrolysis of Polyvinyl Chloride

Table 3 summarizes the information on the pyrolysis of polyvinyl chloride without additives. At about 210°C the dehydrochlorination of the polyvinyl chloride occurs at weak points in the polymer chain.¹⁰ At 240°C to 250°C random dehydrochlorination is initiated. This process eliminates most of the available chlorine in the polymer, producing a sequence of conjugated double bonds which cyclize to form benzene and other aromatic compounds. Using different molecular weight polymers produces different benzene yields which indicates a mechanism of intramolecular cyclization initiated at chain ends. The maximum overall yield of benzene and HCl both occurred at 340°C indicating a simultaneous dehydrochlorination and cyclization process.¹¹ The amount of benzene evolved is dependent on the pyrolysis temperature, polymerization temperature, molecular weight of the PVC, and the HCl concentration within the pyrolysis sample.^{11,12} The evolution of HCl and benzene is a time dependent process.¹³ Above 340°C, a char is formed with evolution of polynuclear aromatics, substituted benzenes, and aliphatic hydrocarbons.^{14,15,16,17} Studies with chlorinated polyvinyl chloride showed that the chloroaromatic species and pure aromatics increased with increasing percent chlorination.^{18,19}

Pyrolysis of PVC With Additives

Table 4 summarizes the effects of additives on the pyrolysis of polyvinyl chloride. The published experiments used control measures so that the off-gassed compounds could be attributed to a particular additive. The additives examined in the literature included the general categories of smoke retarders, stabilizers, fillers, processing aids, and plasticizers. The smoke retarders and stabilizers crosslink the polyvinyl chloride forming a char which reduces aromatic production by hindering cyclization and increases aliphatic production.^{20,21} Fillers, such as calcium carbonate and calcium oxide, reduce the HCl concentration by reaction.²² Inert fillers, such as silica, have no effect upon the pyrolysis products. Some additives, including cadmium stearate, acrylate processing aids, and antimony oxide, react with HCl to form compounds that also off-gas.^{20,23,24,25} At 415°C, phthalate plasticizers decompose to form aromatic compounds, such as benzene, toluene, naphthalene, and phthalic anhydride.²¹ At 600°C, more polycyclic aromatic hydrocarbons (PAHs) and substituted benzenes were identified from the decomposition of phthalates with or without the presence of polyvinyl chloride.^{27,28} A possible reaction mechanism for the formation of PAHs from phthalate acid esters involves the decomposition of the phthalate ester to phthalic anhydride. The phthalic anhydride then decomposes to form benzyne, a reactive intermediate, which reacts with other aromatic species present to form larger aromatics.

TABLE 3. SUMMARY OF LITERATURE DATA ON PYROLYSIS OF POLYVINYL CHLORIDE

Ref	PVC Description	Analysis Method	Results
10	Bulk polymer, Rhone Poulenc GB1150	Successive pyrolysis at 5 min intervals from 180°C to 400°C in 10°C increments using a programmed oven with N ₂ flow. Gases were trapped in a metallic loop and analyzed by GC. HCl was measured by coulometry.	1) HCl was evolved between 210°C and 530°C. The maximum rates for HCl and benzene were between 250°C and 270°C. The first stage is elimination initiated at weak points. This is followed by randomly initiated dehydrochlorination at 240°C to 250°C. 2) The overall benzene yield is larger for lower molecular weight indicating a mechanism of intramolecular cyclization initiated at chain ends.
11	Bulk polymerized PVC, Ruco Division, Hooker Chemical Corp.	Successive pyrolysis in helium at 1 min intervals from 160°C to 500°C in 70°C increments using a platinum coil probe connected to GC/MS.	1) The maximum overall yield of HCl and benzene occurred at 340°C. 2) The amount of benzene evolved is reduced by lowering the temperature of polymerization. 3) Lower molecular weight PVC reduces benzene production at lower temperatures and increases char formation.
12	Suspension resin, Ongrovil S155, Borsodi Vegyi	Differential thermal analysis using DuPont 990 Thermoanalyzer. Pyrolysis in oven at 447°C connected to GC.	The rate of benzene evolution is dependent on HCl concentration within the sample during pyrolysis. A thin sample (400 Å) will have a slower rate because of a shorter diffusion path for HCl.
13	PVC	Thermogravimetric analysis using a thermobalance. CO concentration measured by IR gas analyzer.	1) CO begins to evolve at 240°C. 2) From thermogravimetric methods, some HCl was evolved at 205°C, but none was detected during extrusion at 205°C. HCl evolution depends on the pyrolysis time.
14	Commercial grade PVC	Direct insertion probe connected to MS.	At 300°C, HCl and benzene are present. At higher temperatures, char is formed with evolution of substituted aromatics including benzene, naphthalenes, and fluorenes.

Continued...

TABLE 3 (CONT'D)

15	B.F. Goodrich Chemical Co.	Direct insertion probes at 400°C and 1000°C using isobutane, methane, and ammonia.	At 400°C, benzene was detected. At 1000°C, substituted aromatics and polynuclear aromatic compounds were evolved.
16	High molecular wt PVC, Aldrich Chemical Co.	Laser pyrolysis in air and argon. Condensates on glass tube were analyzed using IR, HPLC, PMR, and GC/MS.	Polycyclic aromatic hydrocarbons were the major fraction of the off-gassed compounds. These include phenanthrene, pyrene, naphthalene, and benzo[a]pyrene.
17	PVC resin with Pb ₂ (SO ₄) ₃ , Bell Laboratories	Burned in combustion oven. Smoke particulates were collected on glass fiber filter with withdrawal of vent air. The particulates were extracted and analyzed by HPLC and GC/MS.	1) More medium molecular weight (178-228) than high molecular weight (~250). PAHs were detected. 2) Carcinogens benzo[a]pyrene and 7,12 dimethyl benzo[a]anthracene were identified.
18	Chlorinated Geon 103EP, B.F. Goodrich Co.	Curie point filament connected to MS at 610°C.	Chloroaromatic species increased with increasing chlorine level.
19	Chlorinated Geon 103EP, B.F. Goodrich Co.	Pyroprobe connected to GC/MS at 600°C in helium. Curie point filament connected to MS at 610°C.	Pure aromatics and aromatics with small side groups increased in relative abundance as chlorine level increased. Aliphatics and more aliphatic aromatics decreased as chlorine level increased.

TABLE 4. SUMMARY OF LITERATURE DATA ON ADDITIVE EFFECTS ON PYROLYSIS OF PVC

Ref.	PVC description	Analysis method	Additives examined	Additive effects
20	Geon 103EPF76 resin, B. F. Goodrich Co.	CDS 100 Pyroprobe connected to GC/MS in helium atmosphere at 550°C.	1) Melaminium beta-octamolybdate, copper oxalate (CuC ₂ O ₄) 2) PMMA processing aid 3) Styrene-acrylonitrile copolymer	1) These smoke retarders decreased the volatile aromatic compounds and increased volatile aliphatic compounds. 2) Degradation of the poly(methyl methacrylate) (PMMA) processing aid in the presence of PVC produces aliphatic chlorides. 3) The styrene-acrylonitrile compound decomposes to yield styrene, acrylonitrile, and other unsaturated pyrolyzates which generate smoke.
21	Geon 103EP, Nippon Geon Ltd.	Furnace pyrolysis unit connected to GC. HCl eliminated by NaOH trap. Nitrogen atmosphere at 415°C.	1) Di(2-ethylhexyl) phthalate (DOP) 2) Dibutyltin dilaurate 3) Dibutyltin bis(n-dodecyl mercaptide) 4) Barium stearate 5) Zinc stearate	DOP increased peak heights of benzene, toluene, and styrene. Hexenes and phthalic anhydride were also produced. Small quantities of benzene, toluene, and styrene were present when just DOP was pyrolyzed. The benzene production increases with temperature. Dibutyltin dilaurate decreases the benzene yield slightly. Dibutyltin bis (n-dodecyl mercaptide) decreases the benzene yield slightly. Barium stearate decreases the benzene yield slightly. Zinc stearate significantly reduces the benzene production.
22	Suspension resin by ICI plc, Plastics Division	Differential thermal analysis in air or nitrogen	1) Silica 2) Calcium carbonate 3) Calcium oxide	1) No effect. 2) The calcium carbonate reacts exothermally with pyrolysis-made hydrogen chloride. As the concentration is increased the endothermic pyrolysis is masked by the exothermic reaction. 3) With calcium oxide, the exothermic peak is increased because of the more exothermic reaction.

CONTINUED....

TABLE 4. (CONT'D)

Ref.	PVC description	Analysis method	Additives examined	Additive effects
23	Technical grade	Direct insertion low (400°C) and high (1000°C) temperature probes connected to CI/MS using isobutane, methane or ammonia as carrier gas.	Antimony oxide, Sb_2O_3	The antimony oxide reacts with HCl to produce antimony chloride. This reduces the HCl concentration.
24	Plasticized PVC	Laser pyrolysis connected to MS	Sb_2O_3	Sb_2O_3 reacts with HCl evolved from pyrolysis of PVC to form $SbCl_3$. This reaction reduces the HCl concentration.
	PVC	Pyrolyzed in a furnace with air or nitrogen. Vapor collected in trap and analyzed by X-ray diffraction.	Cadmium stearate	In air, $CdCl_2$ was detected above 500°C. In nitrogen, cadmium was volatilized as metal Cd above 400°C, and formation of $CdCl_2$ began at 500°C.
26	PVC resin	Glass pyrolysis cell at 440°C connected to glass fiber filter to catch particles and a U-tube packed with solid absorbent to trap gas which is volatilized into GC/MS.	1) $Pb_2(SO_4)_3$ 2) Dialkyl phthalate 3) $CaCO_3$ 4) $Al_2O_3 \cdot 3H_2O$ 5) Sb_2O_3	1) The stabilizer increased the volatile portion of the pyrolyzates. 2) The plasticizer decreased the amount of aromatics found in the volatile portion. It also increased the chlorinated and oxygenated aliphatic and aromatic compounds. 3) The $CaCO_3$ also increased the chlorinated compounds. 4) $Al_2O_3 \cdot 3H_2O$ acted as a heat sink by dehydration and produced more particulate matter. 5) Sb_2O_3 seemed to have no effect.

CONTINUED....

TABLE 4. (CONT'D)

Ref.	PVC description	Analysis method	Additives examined	Additive effects
27	Conoco Chemical Company	Residue from stainless steel bomb with asbestos/copper gasket at 600°C was analyzed using GC/MS.	1) Di(2-ethylhexyl) phthalate (DEHP) 2) Dibutyl phthalate (DBP)	1) PAHs included naphthalene, biphenyl, fluorene, anthracene, pyrene, and substituted aromatics. Pyrolysis of DEHP without PVC results in the same types of compounds. 2) PAHs included indene, naphthalene, biphenyl, acenaphthene, and other substituted aromatics. There were fewer pyrolysis compounds produced. Pyrolysis of DBP without PVC results in the same compounds.
28	Geon 103, B.F. Goodrich Co.	Furnace pyrolysis unit with heated gas sampling valve connected to tandem GC/MS system. Pyrolysis carried out at 600°C in helium atmosphere.	1) o-Dihexyl phthalate (DHXP) 2) o-Di-2-ethylhexyl phthalate (DOP) 3) o-Dicapryl phthalate (DCP) 4) o-Diisodecyl phthalate (DDP) 5) Mixed ester butyl benzyl o-phthalate (BuBzP)	1) DHXP decomposes to offgas phthalic anhydride, hexenes, benzene, toluene, and naphthalene. 2) DOP decomposes to C ₈ olefins, benzene, toluene, naphthalene, and phthalic anhydride. 3) DCP decomposes to C ₈ olefins, benzene, toluene, and phthalic anhydride. 4) DDP decomposes to C ₁₀ olefins, C ₁₀ alcohol, phthalic anhydride, benzene, and toluene. 5) BuBzP decomposes to butene, benzene, toluene, benzyl chloride and phthalic anhydride. The benzyl chloride is formed by a secondary reaction of the pyrolysis products of BuBzP with HCl.

PYROLYSIS STUDY

The literature survey did not examine the off-gassing of the additives due to pyrolysis at normal PVC extrusion temperatures, so the temperatures selected for the laboratory data study were 150°C, 300°C, and 600°C. The normal extrusion temperatures for polyvinyl chloride range from 150°C to 210°C, but most of the literature pyrolysis studies were conducted at temperatures above 400°C. The temperatures for the study represent a normal processing temperature of 150°C, a limiting processing temperature of 300°C, and a maximum literature comparison temperature of 600°C. The results of this study should not be applied to other polymers because of the different types and quantities of additives, diffusional properties of the polymer, and synergetic effects due to the degradation of PVC.

Experimental Equipment and Conditions

The pyrolysis of commercially-supplied polyvinyl chloride samples was conducted using a pyrolysis probe connected to a tandem gas chromatograph/mass spectrometer. Samples of 0.5 mg to 1 mg were weighed using a microbalance (Cahn Electrobalance Model 6). The samples were transferred into quartz tubes (1 inch long and 0.1 inch in diameter) which were inserted into a Chemical Data System Inc. (CDS) platinum coil probe (Model 120). The pyrolysis probe was inserted into a heated interface coupled to the injector of a Tracor 560 gas chromatograph interfaced to a Finnegan 3623 mass spectrometer. The samples were pyrolyzed for ten seconds in helium at one atmosphere. The heating rate was 1000°C/s, and studies were conducted for each sample at 150°C, 300°C, and 600°C. The pyrolyzates were swept onto the column by a helium carrier gas at a rate of 1 mL/min and eluted through 30 m of a 0.25 mm inner diameter DB-5 fused silica capillary column. After two minutes at 30°C, the column temperature was increased at a rate of 10°C/min until the final temperature of 295°C was reached. The pyrolysis products were identified by comparison to the Finnegan software library spectra which contains spectra for over 42,000 compounds. The PVC samples were weighed after pyrolysis to obtain the percent weight loss.

Quality Assurance Plan

The pyrolysis experiments were conducted in accordance with the approved quality assurance project plan (Appendix C). The electro-balance was calibrated daily and verification was performed each time a sample was weighed by weighing Class S calibration weights and recalibrating as necessary. The spectrometer mass assignment was calibrated daily with perfluoro tributylamine. Blanks and external standards of naphthalene and phthalate were pyrolyzed each day prior to pyrolysis of samples. The pyrolyzate components were quantitated by injecting known amounts of the external standards into the pyrolysis interface

and comparing the areas under the gas chromatography peaks with those of the sample pyrograms. To improve reproducibility, this external standard method was used instead of the internal standard method described in the quality assurance plan. The only other deviation from the QA plan was the change of the initial column temperature from 35°C to 30°C. The precision of the analytical methods was calculated as the percent difference between duplicate sample results.

$$\% \text{ Difference} = \frac{\frac{\text{Sample 1 result}}{\text{wt. Sample 1}} - \frac{\text{Sample 2 result}}{\text{wt. Sample 2}}}{\left(\frac{\text{Sample 1 result}}{\text{wt. Sample 1}} + \frac{\text{Sample 2 result}}{\text{wt. Sample 2}} \right) / 2} \times 100$$

The accuracy was calculated as the percent recovery of the off-gassed products.

$$\% \text{ Recovery} = \frac{\text{Wt. of off-gassed compounds detected by column}}{\text{Wt. loss of sample}}$$

Experimental Results

Table 5 presents the percentage weight loss after pyrolysis for the five samples at 150°C, 300°C, and 600°C. At 150°C, the only samples that showed weight losses were the pipe extrusion resin and window profile resin. At 300°C, all of the samples experienced significant weight losses ranging from 32 to 58 percent. The engineering resin had the greatest weight loss; the pipe extrusion resin had the smallest weight loss. At 600°C the weight loss for the samples increased slightly over that for 300°C, the 600°C weight losses ranged from 56 to 75 percent. The engineering resin had the greatest weight loss; the wire jacketing compounds had the smallest weight losses.

TABLE 5. AVERAGE WEIGHT LOSS OF PVC SAMPLES AFTER PYROLYSIS

Sample	Average Percentage Weight Loss		
	150°C	300°C	600°C
Wire Jacketing Compound 1 (PPR-T2-1)	0	57	61
Wire Jacketing Compound 2 (PPR-T2-2)	0	46	56
Engineering Resin (PPR-T2-3)	0	58	75
Pipe Extrusion Resin (PPR-T2-6)	6.9	32	71
Window Profile Resin (PPR-T2-7)	<u>6.7</u>	<u>48</u>	<u>71</u>
Average	2.7	48	67
Standard Deviation	3.3	7.4	6.6

At 300°C, pyrolysis of the polyvinyl chloride samples produced hydrochloric acid, unsaturated hydrocarbons, intact phthalates, and some aromatic compounds. Table 6 presents a summary of the off-gassed components at 300°C for each PVC sample. The amounts represent an average of the values for the two duplicate samples. Appendix D contains more detailed identifications of compounds for each sample including duplicate samples. Pyrolysis of the engineering resin (PPR-T2-3), containing only small amounts of a stabilizer and a lubricant, resulted in off-gassing of hydrochloric acid, unsaturated hydrocarbons, and some aromatic compounds. Pyrolysis of the wire jacketing compounds (PPR-T2-1 and PPR-T2-2) released diheptyl or diisodecyl phthalates, unsaturated hydrocarbons, and 1,2-benzene dicarboxylic acid. Although most of the phthalate off-gassed intact, a small amount of the phthalate degraded by acid hydrolysis to form 1,2-benzene dicarboxylic acid and the corresponding alkenes. The products of pyrolysis of the pipe extrusion resin (PPR-T2-6) included branched saturated hydrocarbons, benzoic acid, and an alkyl benzene resulting from the degradation of the copolymer. The products of the pyrolysis of the window profile resin (PPR-T2-7) included hydrochloric acid, unsaturated hydrocarbons, and aromatic compounds from the degradation of the polyvinyl chloride and the impact modifier.

TABLE 6. SUMMARY OF OFF-GASSED PRODUCTS AT 300°C,
HELIUM ATMOSPHERE

SwRI ID# PPR-T2 Compound	Amount (ng/mg)				
	-1	-2	-3	-6	-7
Unsaturated hydrocarbons	5454	7484	73	---	1462
Diheptyl phthalate	4390	---	---	---	---
Diisodecyl phthalate	---	84870	---	---	---
1,2-benzenedicarboxylic acid	155	209	14	124	---
Hydrochloric acid	---	---	504	---	1893
Benzene	---	---	---	---	46
Alkyl benzene	---	---	---	242	---
Benzoic acid	---	---	58	285	439
Naphthalene	---	---	41	---	---
Branched saturated hydrocarbons	---	67	---	1725	---
Acetic acid, alkyl ester	---	---	---	---	96
Unknown hydrocarbons	981	---	---	---	---
Monochlorinated hydrocarbons	1097	---	---	---	---
Unknown aromatic	75	177	---	---	---
Unknown	248	---	227	138	504
% Recovery	2.2	20.6	0.3	0.8	1.2

At 600°C pyrolysis of the polyvinyl chloride samples produced hydrochloric acid, unsaturated hydrocarbons, intact phthalates, and more aromatic compounds. Table 7 presents a summary of the off-gassed components at 600°C for each PVC sample. Appendix D also includes the detailed identifications for the duplicate runs of each sample. The off-gassed compounds at 600°C were similar to the compounds observed at 300°C except for the addition of more aromatic compounds caused by the cyclization of the polyvinyl chloride. The aromatic compounds produced included benzene, toluene, and naphthalene.

TABLE 7. SUMMARY OF OFF-GASSED PRODUCTS AT 600°C,
HELIUM ATMOSPHERE

SwRI ID# PPR-T2 Compound	Amount (ng/mg)				
	-1	-2	-3	-6	-7
Unsaturated hydrocarbons	25689	48894	375	---	1793
Diheptyl phthalate	322014	---	---	---	---
Diisodecyl phthalate	---	463749	---	---	---
1,2-benzenedicarboxylic acid	12511	7977	712	1853	---
Hydrochloric acid	---	---	---	---	2754
Benzene	11174	5393	19849	17467	17958
Toluene	1902	1578	2097	4165	2107
Alkyl benzene	1735	989	3188	2975	1842
Naphthalene	2194	1663	4083	2825	2503
Alkyl naphthalene	1927	801	1013	733	1136
Benzoic acid	---	---	---	1500	894
Benzoic acid, alkyl ester	168	4604	---	---	---
Benzoic acid, hexyl ester	208	---	---	---	---
Phenanthrene	---	---	215	---	---
2-propenoic acid, 2-methyl methyl ester	---	---	---	763	7353
2-propenoic acid 1-methyl propyl ester	---	---	---	---	630
Formic acid, heptyl ester	3105	---	---	---	---
Branched saturated hydrocarbons	---	---	---	4101	343
Unknown hydrocarbons	4931	---	---	---	---
Monochlorinated hydrocarbons	7234	---	---	---	---
Unknown chlorinated	---	---	38	---	---
Unknown aromatic	988	322	100	---	819
Unknown	2717	55	1943	---	836
% Recovery	66.5	103.3	4.5	5.1	5.9

Discussion of Results

At 150°C the small weight losses of 6.7 to 6.9 percent seem to indicate the off-gassing of small amounts of additives. Because no off-gassing occurred for the other samples which also contained stabilizers, lubricants, and fillers, this small weight loss was attributed to the copolymer and impact modifier. The weight loss was too small to identify or quantitate the off-gassed components. At 300°C and 600°C, most of the weight loss was attributed to the dehydrochlorination of the polyvinyl chloride. The engineering resin, which contained only small amounts of a stabilizer and lubricant, was chosen as a control to represent pure polyvinyl chloride. The weight loss for this control was attributed to the degradation of the polyvinyl chloride by dehydrochlorination and cyclization. The smaller weight loss for the compounds with additives was explained by two factors: (1) if the additives do not off-gas, the weight loss is reduced by diluting the effect of the dehydrochlorination of the polymer and (2) if a calcium based filler is present, it reacts with HCl reducing the weight loss.

The degradation products for the polyvinyl chloride samples were similar to the PVC degradation products reported in the literature.¹⁰⁻¹⁹ At 300°C, PVC degraded by dehydrochlorination to form hydrochloric acid, unsaturated hydrocarbons, and some aromatic compounds. Hydrochloric acid was not identified in many of the samples. This phenomenon could be explained by two possibilities: (1) the hydrochloric acid reacts with a filler or other additives and does not off-gas or (2) the hydrochloric acid elutes too early from the gas chromatograph to be detected. This last problem could be solved by making duplicate runs using a separate column to detect hydrochloric acid and other more volatile components which have early elution times. The process of producing benzene by dehydrochlorination and cyclization of PVC is a time dependent process, so the small amount of benzene detected could be explained by the change in pyrolysis time from one minute in the literature to ten seconds in this study. To simulate the extrusion process, the pyrolysis time should represent the residence time of the additive in the melting zone of the extruder. This residence time depends on the mass flow rate which is dependent on the type of end product and the size of the extruder. The ten second pyrolysis time was chosen because the polymer melt should be heated for only a short time in the extruder.

Even at 600°C, pyrolysis of the wire jacketing compounds, which contained phthalate plasticizers, did not result in detection of polynuclear aromatic compounds as reported in the literature. A small portion of the phthalates degraded to form 1,2-benzenedicarboxylic acid and the corresponding alkenes, but most of the phthalates off-gassed intact without degradation. The mechanism for the formation of polynuclear aromatics from

phthalates involves the degradation of the phthalate to benzyne, a reactive intermediate, which reacts with other aromatic compounds to produce polynuclear aromatics. This complicated mechanism requires time to form the intermediate and then build the larger aromatic compounds. The ten second pyrolysis time compared with the one to ten minute pyrolysis time cited in the literature could account for the absence of the higher molecular weight aromatic compounds.

1,2-Benzenedicarboxylic acid was detected in some samples which did not contain phthalate plasticizers. This is believed to be caused by the development of stagnant zones in the interface between the pyrolysis probe and the column. The components built up in these stagnant regions and then were swept onto the column in future runs.

Quality Assurance Results

The precision and accuracy for each sample are reported on the individual identification sheets contained in Appendix D. The precision, characterized by the percent difference between duplicate runs, varied from 1 to 200 percent. The high percent differences between duplicate runs was attributed to the lack of homogeneity of the samples. The precision could be increased by using larger more representative samples, using a separate column to determine the amounts of noncombustible gases, and removing hydrochloric acid from the pyrolyzates by placing molecular sieves in the effluent line to reduce degradation of the column. The accuracy, measured by the percentage of off-gassed materials recovered, ranged from 0.2 to 181.1 percent. The low percentage of off-gassed materials recovered was caused by the low efficiency of transfer across the pyrolysis interface. The efficiency was measured by injecting naphthalene and phthalate standards into the pyrolysis interface and comparing with the results of standards injected directly into the gas chromatograph. Only 3.0 percent of the naphthalene standard and 0.2 percent of the phthalate standard reached the gas chromatograph through the pyrolysis interface. This low transport across the interface was attributed to stagnant zones in the region between the pyrolysis interface and the gas chromatograph column, and condensation of the volatile components on the insert surfaces. The transport efficiency could be increased by increasing the carrier gas flow rate to reduce stagnant regions, increasing the heating of the interface to decrease condensation, and increasing sweep time to make sure that all of the volatiles have been swept onto the column. The accuracy could also be increased by measuring the GC response factors for each component using pure compounds instead of assuming similar response factors based on naphthalene and phthalate standards.

SUMMARY

The results of the laboratory data study were that little or no off-gassing occurred at normal extrusion temperatures. Most extruders are never heated over 210°C because the polyvinyl chloride begins to degrade reducing the quality of the final product, so limited off-gassing can be expected during normal PVC extrusion operation. As the temperature was increased to 300°C, pyrolysis of the polyvinyl chloride samples resulted in significant weight losses. Most of this weight loss was due to the degradation of the polyvinyl chloride, but some off-gassed compounds were attributed to the presence of additives. The two phthalate plasticizers off-gassed intact or degraded to form 1,2-benzenedicarboxylic acid. The copolymer in the pipe extrusion resin (PPR-T2-6) resulted in off-gassing of branched saturated hydrocarbons, benzoic acid, and an alkyl benzene. The impact modifier in the window profile resin resulted in off-gassing of unsaturated hydrocarbons and benzoic acid. The polyvinyl chloride samples at 600°C off-gassed similar compounds.

The quantity and types of off-gassed compounds due to additives should not be considered as representative of all additives within the specified category of additives, such as plasticizer. The potential for each additive to off-gas or degrade to form off-gassed compounds is dependent on its chemical structure and properties. The most important property to consider is the physical state of the additive at the pyrolysis temperature: solid, liquid, or gas. For example, CaCO_3 fillers, which remain solid at 300°C and 600°C, do not off-gas. Phthalate plasticizers, which are liquids at 300°C and gases at 600°C, off-gas intact or degrade to form other gaseous products. Other additives that are solids at the extrusion temperature should not off-gas, but additives that are gases or liquids with high vapor pressures might off-gas depending on the additives diffusion properties in polyvinyl chloride.

The actual amount of specific additives off-gassed in this study should not be considered to represent the amount of the chemical off-gassed into the workers' environment during extrusion. The amount of chemical off-gassed into the workers' environment depends on this theoretical maximum amount and controls used to limit worker exposure. Many extruders contain devolatilization sections where volatile components are removed from the extruder by a vacuum. Ventilation controls, such as local exhaust systems over exposure sources, also removes some volatiles from the workplace. Because of the short off-gassing time to the workers' environment, the exposure level is limited by the diffusion of the additive to the surface of the extrudate.

SECTION 6

EQUIPMENT MANUFACTURER SURVEY

GENERAL

The equipment manufacturer survey was conducted to obtain information about extrusion processing parameters. Manufacturers and suppliers of extruders and downstream equipment were contacted to obtain information on the different processing variables, such as operating temperatures, flow rates, and cooling systems. The task also included attending a Killion Extruders, Inc. laboratory workshop on extrusion processing. Information on different types of equipment, equipment configurations, and possible exposure sources was obtained during this workshop.

The first part of this section reviews the two different types of PVC formulations, applications for the different formulations, and different processing variables based on application and formulation. The second part details the types of extruders and downstream equipment that are used to cool, postform, collect, and cut the extrudate.

FLEXIBLE AND RIGID FORMULATIONS

Polyvinyl chloride is processed using either rigid or flexible formulations. Rigid formulations usually contain only 5-20% additives, whereas, flexible formulations contain 20-60% plasticizer in addition to other additives. The plasticizers, such as phthalate esters, lower the melt viscosity reducing the necessary processing temperature. Both types of formulations contain heat stabilizers to reduce thermal degradation of the polyvinyl chloride. Fillers are used in both types of formulations to reduce the cost, smooth surface irregularities, and improve stability. Rigid formulation additives also include internal and external lubricants, polymeric processing aids, and impact modifiers. Internal lubricants are blended in the PVC and reduce the viscosity. External lubricants form a layer on the metal surface of the extruder reducing sticking to minimize the possibility of degradation. Polymeric processing aids, such as methacrylate, improve the flow properties by reducing the viscosity. Rigid PVC is a strong, but brittle material, so impact modifiers are used to enhance the resistance of polyvinyl chloride to impact. Both types of formulations may also contain

small amounts of specialized additives, such as liquid stabilizers, fungicides, flame retardants, antioxidants, and colorants. Table 8 contains a list of different types of additives, examples of each type, and typical percent levels used.

TABLE 8. PVC ADDITIVES

Class	Examples	Percent Amounts
Flexible		
Plasticizers	Adipates, azelates, Epoxy 59, phthalates, polyesters, trimelletes, phosphates, glutarates, stearates	20-60
Rigid		
Processing aids	Acrylic copolymers, acrylonitrile butadiene resins, chlorinated polyethylene, polymethyl methacrylate copolymers	0-10
Impact modifiers	Acrylic copolymers, acrylonitrile-butadiene-styrene resins, ethylene-vinyl acetate copolymers, fumaric ester copolymers, chlorinated polyethylene, methyl methacrylate copolymers	5-15
Lubricants	Lead/calcium soaps, ethylene bis-stearamide, fatty acid esters, cumyl phenol benzoate, and petroleum and amide waxes	0-5
Flexible and Rigid		
Heat stabilizers	Lead compounds, metal soaps (barium, cadmium, calcium, and zinc), organotin compounds, antimony compounds, auxiliary organic compounds (organic phosphites, polyhydric alcohols, nitrogenous compounds)	3-10
Inert fillers	Calcium carbonate, talc, carbon black, titanium dioxide, silica	0-40
Light stabilizers	Benzophurones, benzotriazoles, salicylates, substituted acrylonitriles, substituted phenol esters	0.2-0.5
Fungicides	Organotins, quaternary ammonium compounds, arsenicals, copper compounds, phthalimides	
Flame retardants	Phosphate esters, halogenated hydrocarbons, antimony trioxide, melaminum betaoctamolybdate, copper oxalate, alumina trihydrate	0-15
Antioxidants	Bisphenol A, hindered phenols	
Colorants	Organic and inorganic colorants (can contain lead, chromium, cadmium, and mercury)	0-5

Applications

Polyvinyl chloride is used in many different applications because of its low cost, chemical and corrosion resistance, physical strength, and electrical properties. Rigid polyvinyl chloride compounds are typically used in building and structural applications because of their high strength and stiffness. The major application for rigid PVC is pipe which is used for water and gas distribution, drainage, and industrial applications. Other applications for rigid PVC include electrical conduit, window frames, siding, gutters, bottles, packaging, and phonograph records. Flexible PVC is also used in building and structural applications, including flooring, electrical wire and tape, and weather stripping. Other applications include shower curtains, window shades, garden hose, toys, and plastic food wrap.

Extrusion Processing Variables

Flexible compounds are easier to process than rigid compounds, because of the lower melt viscosity. Processing temperatures for flexible compounds range from 150°C to 190°C depending on the level of plasticizer. Processing temperatures range from 180°C to 210°C for rigid compounds. Rigid compounds operate at low flow rates, low shearing, and higher pressures because of the higher melt viscosity and greater possibility for thermal degradation. Both types of formulations are used in different extrusion processes, including wire coating, compounding, and pipe, profile and sheet extrusion. In wire coating, a cross-head die, where the polymer enters at a 90 degree angle from the wire, is used to coat the heated wire with plasticized PVC, which insulates the wire. The line speed for wire coating ranges from 1,000 to 1,500 m/min. In compounding, twin screw extruders are often used to form pellets of polymer blended with additives. These pelletizers operate at speeds of 450 to 7,000 kg/hr. Rigid pipe extrusion involves using a die with an internal mandrel to form the hollow pipe. The extrusion rates vary from 100 to 1,100 kg/hr, depending on the size of the pipe. Both rigid and flexible PVC are used in profile and sheet extrusion. The rigid profile extrusion rates vary from 20 to 200 kg/hr, depending on the complexity of the profile.

Other Processing Techniques

Polyvinyl chloride is also processed by such techniques as injection molding, compression molding, blow molding, and calendering. Both rigid and flexible compounds can be handled in reciprocating screw injection molding units. Flexible compounds are easily processed in injection molding units because of the low melt viscosity, but for rigid compounds, the higher melt viscosity causes a high extruder pressure of 12,000 to 15,000 psi. Compression molding is used mainly to produce phonograph

records from a rigid PVC formulation containing a vinyl acetate copolymer. The blended polymer is fed to the record press in a molten state or as softened pellets, and pressed in the mold at about 2,000 psi. Blow molding of rigid PVC is used to produce bottles. The blow molding process involves continuous extrusion or a reciprocating screw system to produce a tubular extrudate which is blown into the shape of a bottle mold. PVC bottles can be produced at the rate of 2,500 bottles per hour. The calendering process produces high quality flexible or rigid film at high speeds of about 100 m/min. The film is subjected to temperatures greater than 200°C on the last roller because of the high shearing rate.

EQUIPMENT CONFIGURATION

A typical extrusion line consists of a single or twin screw extruder, a profile die, a cooling device, a collection device, and a cutter or winder. The extruder conveys solids from the hopper, melts the polymer, and pumps the melt through the die. The cooling system post-forms and solidifies the extrudate. The collection device pulls the extrudate from the cooling system and delivers it to the cutter or winder. The cutter cuts the extruded item to the desired length, or a winder winds extruded sheet or film onto a roller.

Extruder

The extruder, the main component of the extrusion line, consists of three sections: the solids conveying zone, the melting zone, and the pumping zone. The particulate solids are gravity fed from the hopper into the screw channel. In the first section, the solids are conveyed and compressed by the rotating motion of the screw. The solids are conveyed to the melting zone where heat from the extruder barrel and from shear at the barrel wall melts the polymer blend. The melt is then transported down the extruder barrel to the pumping or pressurization zone. The tight wall clearance and shallow channels increase the pressure in the last section and force the extrudate through the die.

Many extruders also contain a devolatilization section where volatile components are removed by vacuum. This devolatilization section occurs after the pumping section and is followed by another pumping section leading to the die. In the devolatilization section, the melt only partially fills the channel allowing volatile components to diffuse to the surface, evaporate into the vapor phase, and exit through a vacuum vent. All twin screw extruders and some single screw extruders are equipped with this devolatilization section. Since twin screw extruders are used extensively in compounding, and in extruding rigid PVC formulations, most compounds are subjected to devolatilization at some time in the polymer processing.

Cooling System

Five different cooling systems are used to solidify and post-form the extrudate: wet free-extrusion, dry free-extrusion, air and spray cooling, wet vacuum-forming, and dry vacuum-forming. The extrudate leaves the extruder at atmospheric pressure and the melt temperature. The extrudate is cooled to room temperature in two stages. In the first stage, the extrudate is post-formed and cooled until it solidifies. In the second stage, the extrudate is cooled to room temperature. The post-forming is limited because shaping at lower temperatures produces residual stresses in the plastic, but guides and supports are used to aid the plastic in retaining its original shape.

The oldest and most common cooling method is wet free-extrusion. The profile is extruded through a die and into a water trough which may contain fixtures and supports to mold and retain the shape of the profile. In a recirculating tank, the cooling water in a reservoir is circulated through a chiller, pumped to a distribution manifold, and collected in the reservoir. In a non-recirculating system, the water from an outside source is pumped directly into the tank and drained off without recirculation. Water troughs cool the extrudate quickly, but the use of water and energy is inefficient. Free-extrusion into a water trough is used for small to medium, solid cross sections made of flexible PVC.

Dry free-extrusion utilizes air as the cooling media rather than water. An air rack supports the extrudate as it passes between blowers which generate a stream of cooling air. These blowers are concentrated in the first section of the air rack to set the extrudate. The air rack cools the extrudate slowly allowing it to be post-formed in this first section. Because of the slow line speed necessary, this system is used to cool rigid and large flexible profile shapes.

Air and spray cooling utilizes water spray and venturi air cooling units to cool the parts quickly and efficiently. A light spray of moisture on the extrudate is evaporated by a high velocity air stream. This system permits slow cooling by air until the profile is set, followed by rapid heat removal due to evaporation to cool to room temperature. The use of evaporative cooling is much more efficient than the conduction-convection cooling in water troughs. This system is used to cool insulating wire and large rigid and flexible profiles.

The dry vacuum-forming system was developed to process hollow profiles. The extrudate passes through calibrators, which are split blocks of steel with the shape of the final product machined on the inside. At various points along the calibrator,

the extrudate is exposed to a vacuum generated by a vacuum pump. The vacuum pulls the extrudate against the calibrator wall forming the desired shape. While the profile is being shaped, it is cooled by cooling water coils in the calibrator. The dry vacuum-former is usually followed by a secondary cooling unit, such as a water trough or air rack. Dry vacuum-forming is used for hollow shapes and intricate profiles for most rigid and some flexible PVC compounds.

The wet vacuum-forming system is similar to the dry vacuum-forming system except that the extrudate is cooled by direct contact with water. The wet vacuum-forming system is a combination of a water trough and a dry vacuum-former. Calibrators are mounted inside of the first part of the water tank. The vacuum in the calibrators is maintained by a vacuum pump or a venturi device. Cooling water in the water trough enters channels in the calibrator, and comes in contact with the extrudate. Once the extrudate leaves the calibrators, the extrudate is cooled to room temperature by the second part of the water trough. The wet vacuum-former can be used for the same types of products as the dry vacuum-former.

Collection Device

The collection device controls the size of the product by controlling the line speed. Accurate and consistent line speed is necessary to meet narrow profile specifications. The collection device is usually operated by a DC drive connected through a gear system to two caterpuller belts which grip the cooled profile and transfer it to the cutter or winder. For flexible PVC materials, neoprene or butyl rubber sponge belts are used to reduce slippage. For rigid PVC materials, solid neoprene or nitrile rubber can be used.

Winder and Cutting Device

The extruded product is collected either by winding or cutting to the desired length. For small flexible profiles or sheet, the product is collected by wind-up units that wind the product onto a roller. The other method involves cutting the profile or pipe to a specified length using a saw or knife cutter. Saws are used to cut heavy rigid PVC profiles. On-demand cutters with a rotating knife are used for flexible and thin-walled rigid profiles. For rigid profiles, a heated blade is sometimes used to produce smooth cuts. For all cutters, the profile must be supported and constrained to prevent distortion during cutting.

SUMMARY

From the information obtained from the equipment manufacturer survey, there are very few sources of exposure. The

extruder is completely enclosed except for the hopper and the extrudate die. Some volatiles may travel back through the solids conveying zone and exit through the hopper. This limited exposure could be controlled by negative pressure ventilation hoods situated over the hoppers. For those extruders with devolatilization sections, the removal of volatiles while still in the extruder could significantly reduce the worker exposure. Once the extrudate leaves the die, the worker would be exposed to the volatile components if an air cooling method was used. If a water trough or vacuum-forming device was used, the volatiles would be transferred to the water or collected by the vacuum system. With an air cooling system, the off-gassing would continue until the extrudate was solidified in the first section. Most air cooled parts are rigid compounds which contain fewer additives than plasticized or flexible compounds. Most flexible compounds are handled by water cooling systems, so the exposure would be very limited.

SECTION 7

INDUSTRIAL DATA SURVEY

The industrial data survey was conducted to obtain information about worker activities and engineering controls used in industry. Walk-through surveys were conducted at three polymer processing facilities. The different types of polymer processing observed included compounding, extrusion, injection molding, blow molding, and compression molding. During the walk-through surveys, the number of workers required for safe operation, worker activities, possible exposure sources, ventilation, and cooling systems were recorded for each process. The purpose of these walk-through surveys was not to quantitate actual exposure levels, but to observe industrial practices.

PLANT A

Plant A, a 30,000 square foot research and development facility, contained seven different polyvinyl chloride processing units. The building had ventilation hoods situated over loading hoppers and near any source of hot PVC extrudate. The normal operating temperature for the single screw extruders was 177°C, but PVC compounds were never processed above 200°C because of PVC degradation. The plant used good housekeeping procedures and good ventilation. The following paragraphs briefly describe each process, the number of workers required, worker activities, ventilation, and possible exposure sources.

High-Speed Mixer

The first process, a high-speed mixer, was used to compound the polyvinyl chloride with different additives. The machinery consisted of a bowl mixing chamber with a high speed motor and blade located at the bottom. The powder was fed into the mixer manually. After the 1 to 2 pound batch was mixed, the blended polymer slid down through a chute at the bottom of the mixer. The mixer was operated by one worker who measured the materials, loaded the hopper, and operated the mixer which required only limited supervision after start-up. Ventilation hoods were situated over the feed and product chute to remove any off-gassed vapors caused by the heat generated from the intensive shear mixing. The worker was exposed to the hot blended polymer on the product chute, but ventilation controls were designed to limit this exposure.

Pelletizer

A pelletizer blended additives into the polymer melt and formed pellets of blended polymer which are used in different types of processing, including extrusion, injection molding, and blow molding. The unit consisted of two single screw extruders, a cooling tower, and a bagging area. A batch of 25 to 50 pounds of polymer and additives was mixed and fed into the hopper of the first extruder. The extrudate from the first extruder fed directly into the second extruder which had a spaghetti die which extruded cylindrical rods of polymer. A cutter assembly cut the rods into small cylindrical pellets. A high pressure air stream carried the soft pellets through a flexible conduit to a cooling tower. After a batch of pellets had cooled for several minutes, the pellets were collected in the bagging area. The pelletizer was operated by one worker who weighed the materials, fed them into the hopper, and supervised the process. To reduce exposure to off-gassed vapors, the die and cutter assembly were enclosed, and ventilation hoods were situated near any hot polymer extrudate.

Wire Coater

In the wire-coating process, extruded polymer coats conducting wire to provide primary electric insulation. The wire-coating line consists of a single screw extruder, a wire-feed controller, a tension controller, a 30-foot cooling water trough, and a take-up spool. The bare wire is unwound by a tension controller, heated, and fed into a crosshead die where the polyvinyl chloride, entering at a 90 degree angle to the wire, coats the wire surface. The coated wire then passes through a cooling water trough and is collected on the take-up spool. Although the process was not in operation, an estimation of 4 to 5 workers for operation was made based on the complexity of the process. The only source of worker exposure was the distance between the die and the cooling water trough. The fast line speeds of 400 to 1,800 m/min, combined with the short separation distance between the extruder and the cooling water trough, limited the exposure time for a particular segment of the wire.

Sheet Extruder

The sheet extrusion system consisted of a single screw extruder, an air collection system, a draw off unit, and a cutter. A 4-inch wide sheet of PVC, extruded at 163°C and 2,000 psig, was collected on a perforated support plate through which air was blown onto the bottom of the sheet. Overhead air tubes also cooled the top of the sheet. One worker loaded the hopper, checked the extrusion temperature, pressure, and hopper level, and inspected the finished product. The worker was exposed to the hot extrudate as it left the die and cooled in the air

collection system. Ventilation hoods over the hopper and the distance between the die and the air collection trough were designed to limit the exposure to off-gassed vapors.

Pipe Extruder

The pipe extrusion process consisted of a single screw extruder, a wet vacuum-calibrator, a water cooling trough, a draw off unit, and a cutter. The hot pipe leaving the extruder was sized in a 10-foot wet vacuum-calibrator to maintain outer diameter specifications. After the calibrator, the pipe cooled in a 20-foot water trough. One worker loaded the hopper, checked the extrusion temperature, pressure, and hopper level, and collected and inspected the product. The only exposure source was the 2 to 3 inch distance between the die and the calibrator. Ventilation hoods over the hopper and area between the die and the calibrator were designed to reduce worker exposure.

Injection Molding

The injection molding process consisted of a reciprocating screw extruder and a molding chamber. As the screw rotated, it melted the polymer and transported it down the extruder barrel. The screw then moved forward injecting the molten polymer into the mold. The polymer froze at the gate, the narrow entrance to the mold, isolating the mold from the extruder. The screw moved backward, while rotating, allowing the molten polymer to collect in the barrel in front of the screw. When enough melt accumulated in the barrel, the screw stopped. The solidified part was manually ejected from the mold, and the cycle began again. One worker supervised the extrusion process, ejected and stacked the product, and inspected for product quality. At no point was the worker exposed to the hot extrudate.

Blow Molding

The blow molding process consisted of a single screw extruder, a cutter, an air injector, and a two-piece mold. The extruder produced a tubular extrudate. The mold then clamped the tubular extrudate, and the air pushed the hot extrudate against the mold walls producing a bottle. The bottle cooled and was ejected, and the cycle began again. One worker loaded the hopper, operated the extruder, and collected the product. The entire mold area was enclosed within a negative pressure ventilation chamber which collected any off-gassed vapors, so there were no sources of exposure to the hot extrudate.

PLANT B

Plant B, a 50,000 square foot metal building, produced custom profile extrusion materials from flexible and rigid PVC. The facility contained ten single screw extruders along with

water collection troughs, draw off units, and cutters. The extruder was separated from the water collection trough by approximately six inches. For each extrusion unit, one worker started the unit, checked that the collection and cutter devices were in order, and proceeded with the operation of the machinery. One worker loaded the hoppers for all of the extruders, and another worker collected the pieces and transported them to the shipping area. The only source of exposure to the hot extrudate was the short distance between the extruder and the water collection trough. General room ventilation was observed, but no specialized exhaust systems were utilized.

PLANT C

Plant C contained twenty-five reciprocating screw injection molding units which processed polyethylene, polypropylene, rigid and flexible polyvinyl chloride, and polycarbonate. The building contained one 25-ton unit, four 15-ton units, and twenty 10-ton units. The injection molding units were operated automatically, so only one worker was required for four units. The worker would load the hoppers and then inspect the product for quality. The worker was not exposed to the hot extrudate at any time during the process. General room ventilation was observed, but no specialized exhaust systems were utilized.

SUMMARY

During the walk-through surveys, the worker exposure to additives off-gassed during the processing of polyvinyl chloride was very limited. The most noticeable source of exposure occurred during start-up of the extrusion operation when the worker would manually support and guide the extrudate into the cooling system. For normal operation, the worker was exposed to the hot extrudate in the small area (1 to 6 inches) between the die and the cooling system. For a water or vacuum cooling system, the worker exposure ended as the extrudate entered the cooling system. For natural or forced air convection cooling devices, the exposure continued until the product solidified. Of the extrusion processes observed, air cooling was only used in the case of sheet extrusion. During injection, compression, and blow molding, the worker was never exposed to the hot extrudate. Most compounding processes occurred in enclosed, automated systems with ventilation controls to limit the exposure to the worker. In all cases, additional ventilation controls could be utilized to reduce even the limited worker exposure that did exist.

The worker scenarios for the different extrusion processes were similar. At the start-up of the procedure, the extrudate was manually supported and guided into the cooling device and puller. The worker would load the hopper; check the hopper level, on-line gauging system, and extrusion temperature and

pressure; collect the product; and inspect for product quality. Product quality control involved monitoring an on-line gauging system for dimensions of the product or manually measuring the dimensions. The surface quality of the product was also examined for defects, such as die marks, the sharkskin or chatter effect, orange peel appearance, or surface burning. These problems could be solved by proper adjustment of the extruder operating conditions. The worker spent most of his time either at the end of the extrusion line where the product was examined or at the control panel on the extruder observing operating parameters.

SECTION 8

WORKER EXPOSURE MODEL

The purpose of this research study was to develop a theoretical model to predict the worker exposure during PVC extrusion processing due to off-gassing of additives. Based on reasonable worst case assumptions, a model to determine the generation rate from the hot extrudate was derived from mass transport equations. A Gaussian plume dispersion model is included to estimate the concentration of the chemical in the workers environment from the generation rate. This section presents methods to estimate the important parameters necessary to evaluate the worker exposure from the two models. This model does not attempt to account for worker exposure due to particulate emissions during extrusion.

GENERATION RATE MODEL

To represent the reasonable worst case, the model for the generation rate was derived from the transport equations governing diffusion in a large, flat slab. Because the body of the extruder is enclosed, the only possible exposure sources are the feed hopper and the hot extrudate leaving the extruder. For the purposes of this model, the small amount of volatile gas escaping back through the feed hopper is neglected. The geometry of a large, flat slab was chosen to represent a reasonable worst case and simplify the calculations. If necessary, the generation rate for different geometries could be approximated using the surface area to volume ratio. In the extruder, the chemical additive may volatilize or degrade to form gaseous products. As the extrudate leaves the extruder, the mixing action of the rotating screw should uniformly distribute these volatiles in the extrudate. Although the slab is moving between the extruder and the cooling system, it can be modeled as a stationary slab that is exposed for the time equivalent to the moving slab's travel time between the extruder and the cooling system. Assuming diffusion in only one direction, the partial differential equation describing this unsteady state diffusion is:

$$\frac{\partial \rho_A}{\partial t} = D_A \frac{\partial^2 \rho_A}{\partial z^2} \quad (1)$$

where ρ_A = mass concentration of additive in the extrudate

D_A = mass diffusivity of additive in the extrudate

t = time

z = direction perpendicular to the flat surface

To find the concentration in the slab as a function of time and position, this equation was solved by the method of separation of variables with the following initial and boundary conditions:

Initial Condition

$$\rho_A(z, 0) = \rho_{AO}$$

Boundary Conditions

$$\rho_A(0, t) = 0$$

$$\rho_A(L, t) = 0$$

where ρ_{AO} = initial additive mass concentration

L = thickness of slab

The initial condition assumed a uniform mass concentration, ρ_{AO} , in the extrudate leaving the extruder. The boundary conditions were specified assuming an immediate surface evaporation rate. Solving this equation for the generation rate, G , results in the following equation²⁹:

$$G = \frac{QV}{L} = w_{AO}m' - \frac{8w_{AO}m'}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp \left[-D_A \frac{(2n+1)^2 \pi^2}{L^2} t_f \right] \quad (2)$$

where V = volumetric flow rate

w_{AO} = initial volatile weight fraction of additive

m' = mass flow rate

Q = amount of chemical generated per unit area

t_f = off-gassing time

Assumptions

Some discussion of the assumptions used in deriving this model is necessary to evaluate the effectiveness of this model in estimating the generation rate. The assumptions made in deriving this model were:

1. constant density, ρ
2. constant diffusivity, D_A
3. uniform initial mass concentration, ρ_{AO}
4. no convective flow
5. diffusion only in the z-direction
6. Fickian diffusion which neglects diffusion due to temperature and pressure gradients or external forces
7. no chemical reaction
8. immediate surface evaporation

The extrudate leaves the extruder at the melt temperature and is subsequently cooled during the off-gassing period. As the extrudate cools, the density increases and the diffusivity decreases. These conditions cause a decrease in the generation rate, so the assumptions of constant density and diffusivity should provide a conservative estimate. If a more realistic model is desired, an average or log mean average temperature could be used to calculate the diffusivity.

The assumption of a uniform initial concentration is valid because the rotation of the screw should mix the additives uniformly into the extrudate. If the slab is considered to be stationary for the time, t_f , that the extrudate flows between the extruder and the cooling device, the assumption of no convective flow is valid. The assumption of unidirectional mass transfer is valid, if the small diffusion in the direction of flow is ignored. The sections that leave the extruder first will have a lower concentration because of the longer off-gassing time, so a slight concentration gradient will develop in the direction of flow.

The assumption of Fickian diffusion neglects any diffusion due to temperature or pressure gradients, and external forces. The Soret effect, diffusion due to a temperature gradient, is usually small and can be neglected. There was no pressure gradient to be considered, and the external force of gravity can be neglected. The assumption of no chemical reaction is valid for additives that do not degrade during the extrusion process. For those additives that do degrade to form volatile products, the rate of production of a volatile compound should be accounted for by some reaction rate law. The boundary conditions were specified assuming an immediate surface evaporation rate. The surface evaporation rate could be modeled assuming a boundary layer of the additive on the surface of the extrudate, but an immediate surface evaporation rate simplifies the model and represents the worst case.

Series summation

The tedious process of summing the series can be simplified by rearranging the equation and recognizing that G/w_{AOM}' is a function of only one dimensionless variable, DAt_f/L^2 .

$$\frac{G}{w_{AOM}'} = 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp \left[-D_A \frac{(2n+1)^2 \pi^2}{L^2} t_f \right] \quad (3)$$

Using a LOTUS 1-2-3TM spreadsheet, individual terms of the series were generated and summed for different values of the dimensionless variable, DAt_f/L^2 , ranging from 0 to 1. Table 9 presents values of G/w_{AOM}' for various values of DAt_f/L^2 .

TABLE 9. VALUES OF G/w_{AOM}' FOR VARIOUS DAt_f/L^2 VALUES

DAt_f/L^2	$\log DAt_f/L^2$	G/w_{AOM}'	$\log G/w_{AOM}'$	Number of terms included in summation
0		0.000		1000
1×10^{-10}	-10	0.000		1000
1×10^{-9}	-9	0.000		1000
1×10^{-8}	-8	0.000		1000
1×10^{-7}	-7	0.001	-3.0	746
1×10^{-6}	-6	0.002	-2.7	315
1×10^{-5}	-5	0.007	-2.2	121
1×10^{-4}	-4	0.023	-1.64	45
1×10^{-3}	-3	0.071	-1.15	16
1×10^{-2}	-2	0.226	-0.65	4
1×10^{-1}	-1	0.698	-0.16	1
1	0	1.000	0	1

Appendix E contains the individual terms of the series and the summation values. Using Table 9, G/w_{AOM}' can be calculated for the estimated value of DAt_f/L^2 by interpolation between the log values of DAt_f/L^2 and G/w_{AOM}' . To determine the generation rate from this table, the initial volatile weight fraction, mass flow rate, diffusivity, off-gassing time, and slab thickness must be estimated from the limited information supplied in the PMN system.

ESTIMATION OF VARIABLES

Information on the type of processing is necessary to estimate the variables for utilization of Table 9. The PMN system only requires information on the category of use and additive weight percent in the formulation. The category of use includes information on the type of additive, such as plasticizer, and type of process or end product. This information is very limited, so certain simplifying assumptions have to be made. The diffusivity, mass flow rate, and off-gassing time are estimated based on the specification or assumption of formulation type. The assumption can be made based on the type of additive or the end use of the product. Rigid formulation additives include heat stabilizers, internal or external lubricants, polymeric processing aids, impact modifiers, fillers, and pigments. Flexible formulation additives include heat stabilizers, plasticizers, fillers, and pigments. Rigid formulation applications include pipe, electrical conduit, window frames, siding, gutters, bottles, packaging, and phonograph records. Flexible formulation applications include flooring, electrical wire and tape, weather stripping, shower curtains, window shades, garden hose, toys, and plastic food wrap.

Volatile Weight Fraction

The weight fraction in the PMN system is the initial weight fraction of the additive in the formulation. The volatile weight fraction must be estimated from the total initial weight fraction. If the PVC melt temperature is above the additive boiling point, then the initial weight fraction should be used. If the additive melting point is above the PVC melt temperature, then the off-gassing will be negligible for the assumption of a low vapor pressure over a solid. If the melt temperature is between the additive melting and boiling point temperature, then some of the additive will be a gas in equilibrium with the liquid. In addition to the percentage of vapor, the volatile fraction also depends on the solubility in the polymer. If there is no data on the solubility in the polymer, the volatile weight fraction calculated based on the vapor pressure can be used as a maximum value.

The initial volatile weight fraction can be calculated using the vapor pressure at the extrudate temperature. The weight fraction must first be converted to a mole fraction so that Raoult's Law may be utilized.

$$x_{AO}^{PMN} = \frac{w_{AO}^{PMN} / M_A}{w_{AO}^{PMN} / M_A + (1 - w_{AO}^{PMN}) / M_P} \quad (4)$$

x_{AO}^{PMN} = initial mole fraction of additive from PMN
 w_{AO}^{PMN} = initial weight fraction of additive from PMN
 M_A = molecular weight of additive
 M_P = molecular weight of PVC

Using Raoult's Law, the initial volatile mole fraction, x_{AO} , equals the vapor pressure multiplied by the initial mole fraction from the PMN in accordance with equation 5.

$$x_{AO} = x_{AO}^{PMN} P^{\circ} \quad (5)$$

x_{AO} = initial volatile mole fraction of additive
 P° = vapor pressure, atm

The volatile mole fraction is then converted to the mass fraction using equation 6.

$$w_{AO} = \frac{x_{AO} M_A}{x_{AO} M_A + (1 - x_{AO}) M_P} \quad (6)$$

The vapor pressure at any temperature, T , can be estimated using the Clapeyron equation if the vapor pressure at two different temperatures is known.

$$P^{\circ} = (P_2/P_1)^b \quad (7)$$

$$\text{where } b = \frac{T_2(T - T_1)}{T(T_2 - T_1)}$$

If the heat of vaporization, ΔH , is known, the vapor pressure at any temperature, T , can be calculated from just one other vapor pressure point.

$$\ln (P^{\circ}/P_1) = \Delta H/R[(1/T_1 - 1/T)] \quad (8)$$

ΔH = heat of vaporization
 R = gas law constant

If the additive degrades to form volatile compounds, the weight fraction of the degradation product would have to be estimated. As a worst case scenario, the weight fraction could be determined from stoichiometry assuming total degradation of the additive.

Mass Flow Rate

The mass flow rate depends on many variables including the screw rotational speed, extruder size, end product, type of formulation, type of cooling system, size of die opening, and temperature. The mass flow rate is an experimental variable that is used to optimize product quality and production rate. Extrusion mass flow rates range from 25 kg/hr for laboratory extruders to 7,000 kg/hr for a large compounding line. Based on the end product, the general guidelines for the mass flow rate established in the equipment manufacturer survey are presented in Table 10.

TABLE 10. EXTRUSION MASS FLOW RATE DATA

Process	Mass Flow Rate (kg/hr)
Flexible Compounds	
General	50-300
Wire coating	0.5-5
Rigid Compounds	
Profile	25-200
Pipe	100-1,100
Pellets	450-7,000

Off-Gassing Time

The off-gassing time depends on the type of cooling system used which depends on the type of formulation and end product. For flexible formulations, water troughs are the most common cooling system. For water troughs the off-gassing time is the time necessary for the extrudate to travel between the extruder and the water bath. The longest distance between the extruder and the water trough observed in the industrial data survey was approximately 6 inches. At a typical low speed of 6 meters per minute, the off-gassing time would be 1.5 seconds. For the wire coating process, the fast line speed of 1,000 meters per minute reduces this off-gassing time to 0.009 seconds. For rigid formulations either air cooling or vacuum-calibrators are used. For rigid solid profiles, air cooling is the typical cooling method. In air cooling, the profile is cooled to the set point in the first 2 to 3 meters of the air rack, but the line speed can be as slow as 1 meter per minute, resulting in an off-gassing time of 120 to 180 seconds. For hollow pipe sections, the off-

gassing only occurs in the small area between the extruder and the vacuum-calibrator. Assuming a 6-inch separation and a line speed of 1 meter per minute, the off-gassing time is 9 seconds. Table 11 summarizes this information on off-gassing times.

TABLE 11. OFF-GASSING TIME

Process	Off-gassing Time, t_f^* seconds
Flexible Compounds	
General	1.5
Wire coating	0.009
Rigid Compounds	
Solid profile	120-180
Pipe	9

* Assuming 6-inch travel distance in the workplace.

Diffusivity

The diffusivity depends on the molecular size and concentration of the chemical additive, the type of PVC formulation, and the processing temperature. The diffusion of gases through a polymer can occur by two different mechanisms depending on the size of the diffusing gas. For simple small molecules, such as hydrogen, diffusion occurs through holes in the polymer matrix. In order for larger molecules to diffuse through the polymer, the polymer chain must move out of place allowing the molecule to pass.

A method of predicting a chemical's diffusivity in a polymer above the glass transition temperature has been developed using a free volume theory.^{30,31} This method requires density and viscosity data for the pure chemical and polymer as a function of temperature, three values of the diffusivity at two different temperatures, and sorption equilibrium data at a single temperature. This detailed information is not supplied by the PMN system, so simpler, less accurate, estimation techniques are included in this section.

Concentration Dependence--

For large molecules, the diffusion coefficient increases with increasing concentration because of the interaction between the polymer and the additive. The larger additives act as

plasticizers which increase the chain mobility thus increasing the diffusivity of all additives present in the formulation. The dependence of the diffusivity on the concentration of dioctyl phthalate at 30°C in PVC is governed by the following equation.³²

$$\ln D_{DOP}^{30} = - \frac{2.34}{w_{DOP}} - 9.7 \quad (9)$$

where D_{DOP}^{30} = the mass diffusivity of dioctyl phthalate in PVC at 30°C (cm²/s)

w_{DOP} = weight fraction of DOP

Because of a lack of information on concentration dependence of other plasticizers, this dependence will be used to approximate the effect of all other plasticizers. To determine the diffusivity of another additive in a plasticized formulation, the diffusivity of the plasticizer is first calculated and then adjusted to account for the difference in additive size.

Temperature Dependence--

The temperature dependence of the diffusivity is frequently approximated using an Arrhenius temperature relation:

$$D_A = D_{AO} \exp (-E_D/RT) \quad (10)$$

where D_{AO} = diffusivity constant for an additive

E_D = activation energy

T = absolute temperature

Although the Arrhenius temperature relation correlates the diffusivity at low temperatures, extrapolation to higher temperatures results in larger errors. From a plot of the diffusivity of argon in PVC films at different temperatures, the activation energy has been calculated as approximately 12 kcal/mole.³³ The activation energy is usually a function of the type of polymer not the diffusing gas, so this value can be assumed to hold for all additives in rigid PVC formulations. In flexible formulations, the temperature effect is much greater. For example, the activation energy for the plasticizer, DOP, is approximately 19 kcal/mole.³⁴ Most of the diffusivity data available in the literature is reported at 25°C or 30°C, but the extrudate emerges from the extruder at 150°C to 210°C. The diffusivity for a given additive at any temperature, T , can be calculated from its diffusivity at a reference temperature, T_{REF} , using the following equation:

$$D_A^T = D_A^{T_{REF}} \exp \left[\frac{E_D}{R} \frac{1}{T_{REF}} - \frac{1}{T} \right] \quad (11)$$

Molecular Volume Dependence--

The dependence of diffusion in polyvinyl chloride on the additive's molecular size has not been previously modeled or correlated. For the purposes of this model, the limited work on diffusivity in liquids based on the Eyring hole theory will be applied to the polymer melt.³⁵ This theory models the liquid as a quasi-crystalline lattice through which molecules diffuse, but does not account for the interaction of larger molecules with the polymer chain. Based on this theory, Wilke and Chang have developed the following correlation for diffusion of nonelectrolytes in an infinitely dilute solution:³⁶

$$\frac{D_A \mu_B}{T} = \frac{7.4 \times 10^{-8} (\Phi_B M_B)^{1/2}}{V_A^{0.6}} \quad (12)$$

where,

D_A = mass diffusivity of A diffusing through liquid B, cm^2/s

μ_B = viscosity of solution, centipoise

V_A = molal volume of additive at normal boiling point, cm^3/gmole

Φ_B = association parameter for solvent B

T = absolute temperature, K

M_B = molecular weight of solvent

This correlation shows that the diffusivity is inversely proportional to $V_A^{0.6}$ at constant temperature. Thus, the diffusivity of the additive can be obtained by multiplying the diffusivity reported for another compound by the ratio of the molal volumes raised to the 0.6 power:

$$D_A = D_{REF} \left[\frac{V_{REF}}{V_A} \right]^{0.6} \quad (13)$$

If the molal volume of the additive is unknown, it can be estimated by adding the atomic volumes of each element present in the molecular formula. Table 12 lists the atomic volume of some common elements. When ring structures are involved, these atomic volume summations need to be corrected for the reduced volume. Table 13 presents a list of these correction factors for common ring structures. For plasticized compounds, the diffusivity can be calculated for dioctyl phthalate at the desired concentration

and then adjusted for molecular size using this correlation. For the diffusion of smaller molecules in rigid compounds, the diffusivity of a gas can be adjusted using this molecular volume correlation from Table 14.

TABLE 12. ATOMIC VOLUMES FOR CALCULATING COMPLEX MOLECULAR VOLUMES FOR SIMPLE SUBSTANCES³⁵

Element	Atomic Volume cm ³ /gmole
Bromine	27.0
Carbon	14.8
Chlorine	21.6
Hydrogen	3.7
Iodine	37.0
Nitrogen, double bond	15.6
Nitrogen, primary amine	10.5
Nitrogen, secondary amine	12.5
Oxygen, except as below	7.4
Oxygen, in methyl esters	9.1
Oxygen, in methyl esters	9.9
Oxygen, in higher esters and other esters	11.0
Oxygen, in acids	12.0
Sulfur	25.6

TABLE 13. CORRECTION FACTORS FOR RING STRUCTURES³⁵

Ring Structure	Volume Correction cm ³ /gmole
Three membered ring	-6
Four membered ring	-8.5
Five membered ring	-11.5
Pyridine	-15
Benzene	-15
Naphthalene	-30
Anthracene	-47.5

TABLE 14. VALUES OF DIFFUSIVITY IN POLYVINYL CHLORIDE
AT 35°C³³

Gas	D _A (cm ² /s)
Ar	2.42 x 10 ⁻⁹
N ₂	1.37 x 10 ⁻⁹
CH ₄	3.31 x 10 ⁻¹⁰
CO ₂	1.45 x 10 ⁻⁹

EXAMPLES OF GENERATION RATE CALCULATIONS

To illustrate the use of these estimations in calculating the generation rate, two examples will be examined. The first example will calculate the generation rate of diheptyl phthalate from PVC. The second example demonstrates the estimation of worker exposure to residual vinyl chloride monomer in a rigid PVC formulation.

Example 1. Diheptyl Phthalate

Diheptyl phthalate (DHP) is used as a plasticizer in flexible PVC compounds at about 30 percent by weight. Because of the interaction between the polymer and the plasticizer, the diffusivity depends on the concentration of the plasticizer. Assuming that the concentration dependence of dioctyl and diheptyl phthalate are similar, the diffusivity can be calculated using equation 9 and then adjusted to account for the molecular volume difference using equation 13. According to equation 9,

$$\ln D_{DOP}^{30} = - \frac{2.34}{w_{DOP}} - 9.7$$

$$\text{For } w_{DOP} = 0.30, \quad \ln D_{DOP}^{30} = - \frac{2.34}{0.30} - 9.7$$

$$D_{DOP}^{30} = 2.51 \times 10^{-8} \text{ cm}^2/\text{s}$$

Applying equation 13,

$$D_{DHP}^{30} = D_{DOP}^{30} \left[\frac{V_{DOP}}{V_{DHP}} \right]^{0.6}$$

The molal volumes of dioctyl and diheptyl phthalate must be calculated using Tables 12 and 13 to use this equation.

$$V_{DOP} = 24V_C + 38V_H + 4V_O \text{ ESTER} - V_{\text{BENZENE CORR.}}$$

$$= 24(14.8) + 38(3.7) + 4(11.0) - 15 = 525 \text{ cm}^3/\text{gmole}$$

$$V_{DHP} = 22V_C + 34V_H + 4V_O \text{ ESTER} - V_{\text{BENZENE CORR.}}$$

$$= 22(14.8) + 34(3.7) + 4(11.0) - 15 = 480 \text{ cm}^3/\text{gmole}$$

$$D_{DHP}^{30} = (2.51 \times 10^{-8} \text{ cm}^2/\text{s}) \left[\frac{525}{480} \right]^{0.6}$$

$$= 2.65 \times 10^{-8} \text{ cm}^2/\text{s}$$

Because flexible formulations are exposed for only a short time, the extrudate is assumed to remain at the melt temperature of 180°C. The diffusivity at 180°C can be calculated using the Arrhenius temperature dependence, according to equation 11 using an activation energy of 19 kcal/mole.

$$D^T = D^{T_{\text{REF}}} \exp \left[\frac{E_D}{R} \frac{1}{T_{\text{REF}}} - \frac{1}{T} \right]$$

$$D_{DHP}^{180} = D_{DHP}^{30} \exp \left[9562 \frac{1}{303} - \frac{1}{453} \right]$$

$$= 2.65 \times 10^{-8} \exp \left[9562 \frac{1}{303} - \frac{1}{453} \right]$$

$$= 9.15 \times 10^{-4} \text{ cm}^2/\text{s}$$

The term $D_{DHP}^{180} t_f / L^2$ must be determined to use Table 9 to solve for the generation rate. Since no information on the type of product is available, a thickness of 2 mm will be assumed to represent the worst case. From Table 11, the off-gassing time for a flexible compound is 1.5 seconds.

$$D_{DHP}^{180} t_f / L^2 = \frac{(9.15 \times 10^{-4} \text{ cm}^2/\text{s})(1.5 \text{ s})}{(0.2 \text{ cm})^2} = 3.43 \times 10^{-2}$$

Interpolation of Table 9 results in the fraction of the maximum possible generation rate, $G/w_{AO} m'$, being 0.410. To solve for the generation rate, the term $m' w_{AO}$ must be calculated. From Table 10, the mass flow rate for a flexible compound can be assumed to be 150 kg/hr. The initial volatile weight fraction can be

calculated using equations 4 through 6 assuming the vapor pressure of DHP at 180°C is equivalent to the vapor pressure of DOP at 200°C which is 0.0237 atm. The first step is to convert the PMN weight fraction of 0.3 to a mole fraction using equation 4.

$$x_{AO}^{PMN} = \frac{(0.3)/(362)}{(0.3)/(362) + (0.7)/(90,000)} = 0.99$$

Using equation 5, the initial volatile mole fraction is then calculated.

$$x_{AO} = (0.99)(0.0237) = 0.0235$$

The mole fraction is converted to the weight fraction using equation 6.

$$w_{AO} = \frac{(0.0235)(362)}{(0.0235)(362) + (0.9765)(90,000)}$$

$$w_{AO} = 9.68 \times 10^{-5}$$

$$G = \frac{G}{m'w_{AO}} m'w_{AO}$$

$$G = (0.410)(9.68 \times 10^{-5})(150 \text{ kg/hr}) = 0.0060 \text{ kg/hr} = 5.95 \text{ g/hr}$$

Example 2. Vinyl Chloride Monomer

This example will estimate the worker exposure for residual vinyl chloride monomer in a rigid PVC formulation. Because rigid formulations are air cooled where the extrudate is exposed for a long time, the diffusivity is evaluated at the average of the melt temperature, 210°C, and the glass transition temperature, 87°C.

$$T = \frac{1}{2} (210 + 87) = 149^{\circ}\text{C}$$

The diffusivity of vinyl chloride in PVC can be estimated by calculating the diffusivity of methane at 149°C and then adjusting for the difference in molal volume in accordance with equations 11 and 13. From Table 14,

$$D_{CH_4}^{35} = 3.31 \times 10^{-10} \text{ cm}^2/\text{s}$$

From equation 11 using an activation energy of 12 kcal/mole,

$$\begin{aligned} D_{CH_4}^{149} &= D_{CH_4}^{35} \exp \left[6040 \frac{1}{308} - \frac{1}{422} \right] \\ &= 3.31 \times 10^{-10} \exp \left[6040 \frac{1}{308} - \frac{1}{422} \right] \\ D_{CH_4}^{149} &= 6.62 \times 10^{-8} \text{ cm}^2/\text{s} \end{aligned}$$

To evaluate the diffusivity of vinyl chloride, the molal volumes of methane and vinyl chloride must be determined. From Table 12 and equation 13,

$$\begin{aligned} V_{CH_4} &= V_C + 4V_H \\ &= 14.8 + 4(3.7) = 29.6 \text{ cm}^3/\text{gmole} \end{aligned}$$

$$\begin{aligned} V_{VCM} &= 2V_C + 3V_H + V_{Cl} \\ &= 2(14.8) + 3(3.7) + 21.6 = 62.3 \text{ cm}^3/\text{gmole} \end{aligned}$$

$$\begin{aligned} D_{VCM}^{149} &= D_{CH_4}^{149} \left[\frac{V_{CH_4}}{V_{VCM}} \right]^{0.6} \\ &= (6.62 \times 10^{-8} \text{ cm}^2/\text{s}) \left[\frac{29.6}{62.3} \right]^{0.6} \\ D_{VCM}^{149} &= 4.24 \times 10^{-8} \text{ cm}^2/\text{s} \end{aligned}$$

From Table 11, the off-gassing time for rigid solid profiles is 160 s. Since no information is available on the process or end product, a thickness of 2 mm will be assumed again. To apply Table 9, the dimensionless variable, D_{At_f}/L^2 , is calculated,

$$\frac{D_{VCM}^{149} t_f}{L^2} = \frac{(4.23 \times 10^{-8} \text{ cm}^2/\text{s}) (160 \text{ s})}{(0.2 \text{ cm})^2} = 1.69 \times 10^{-4} \text{ cm}^2/\text{s}$$

From interpolation of Table 9, the fraction of the maximum possible generation rate, $G/w_{AO}m'$, is 0.030. From Table 10, the mass flow rate for rigid profiles can be assumed to be 200 kg/hr. The concentration of vinyl chloride in the polymer depends on the type of polymerization process and the amount of stripping used to remove residual monomer. For the purpose of this example, the concentration will be assumed to be 0.2 weight percent which represents the proposed regulatory values in 1975.³⁷ Vinyl chloride is a gas at room temperature, so all of the vinyl chloride is assumed to be vapor. Thus,

$$G = \frac{G}{m'w_{AO}} m'w_{AO} = (0.0293)(200 \text{ kg/hr})(0.002) = 0.0117 \text{ kg/hr}$$

WORKER EXPOSURE MODEL

Through the literature search, a Gaussian plume dispersion model to estimate workplace exposure from emission rate data was discovered.³⁸ The maximum concentration as a function of distance from the exposure source is predicted by the following equation:

$$c'_{\max} = 1337.786 \text{ G}/(M \times U) \cdot (1/2\pi\sigma_y\sigma_z) \quad (14)$$

where $c'_{\max}$ = the concentration of the additive in parts per million by volume (ppm (v)) at some distance, d , downwind from the source

G = the quantity of the additive being released in grams per hour

M = the chemical additive molecular weight

U = the velocity of the workplace ambient air passing the point of release in feet per minute

σ_y & σ_z = the diffusion coefficients in meters which are functions of the distance, d , from the source. Table 15 presents values of the function $1/2\pi\sigma_y\sigma_z$ as a function of distance.

TABLE 15. DIFFUSION FUNCTION, $1/(2\pi\sigma_y\sigma_z)^{3/2}$

Distance feet	$1/(2\pi\sigma_y\sigma_z)$ m^{-2}	Distance m'	$1/(2\pi\sigma_y\sigma_z)$ m^{-2}
1.5	0.1458	0.5	0.1447
2.0	0.1420	1.0	0.1326
3.0	0.1347	2.0	0.1020
4.0	0.1259	3.0	0.08120
5.0	0.1166	4.0	0.07074
6.0	0.1072	5.0	0.06217
7.0	0.09929	6.0	0.05507
8.0	0.09288	8.0	0.04528
9.0	0.08653	9.0	0.04188
10.0	0.08069	10.0	0.03789
12.0	0.07431	20.0	0.01989
14.0	0.06844	30.0	0.01255
16.0	0.06324	40.0	0.00938
18.0	0.05873	50.0	0.00793
20.0	0.05451	60.0	0.00642
25.0	0.04912	70.0	0.00553
30.0	0.04131	80.0	0.00463
35.0	0.03521	90.0	0.00426
		100.0	0.00372

This equation is limited to an area where the plume does not reflect from a solid surface. The maximum distance for validity of the correlation is defined by the following equation.

$$h = d_{\max} \tan 8.6^\circ \quad (15)$$

where h = height of source above the floor

$d_{\max}$ = maximum valid distance

This model does not include the effect of exhaust ventilation situated over the hot extrudate. Although exhaust ventilation could significantly reduce the exposure, the Gaussian plume dispersion model should predict a reasonable worst case model.

Example 1. Diheptyl Phthalate

The generation rate for diheptyl phthalate predicted by the generation rate model is 5.95 g/hr.

$$G = 5.95 \text{ g/hr}$$

The molecular weight of diheptyl phthalate is 362 g/mole. From Table 15 for a worker separated from the generation source by 5 feet, $1/(2\pi\sigma_y\sigma_z)$ is 0.1166 m^{-2} . Assuming a velocity of 10 ft/min to represent general room ventilation, the concentration can be calculated from equation 14.

$$\begin{aligned} c'_{\max} &= \frac{1337.786 \text{ G}}{\text{MU}} (1/2\pi\sigma_y\sigma_z) \\ &= \frac{(1337.786)(6.95)}{(362)(10)} (0.1166) \end{aligned}$$

$$c'_{\max} = 0.256 \text{ ppm(v)} = 3.77 \text{ mg/m}^3$$

To check the validity of the use of the following correlation, the distance, d , which is 5 feet, must be less than $d_{\max}$. Assuming a height, h , of 3 feet, $d_{\max}$ is calculated to be 20 feet.

Example 2. Vinyl Chloride Monomer

The generation rate for vinyl chloride as predicted by the generation rate model is 11.7 g/hr. The molecular weight of vinyl chloride is 62.5. A worker separated from the exposure source by a distance of 5 feet will be assumed. Because of the blowers used to cool the extrudate, the air velocity is assumed to be 100 ft/min.

$$\begin{aligned} c'_{\max} &= \frac{1337.786 \text{ G}}{\text{MU}} (1/2\pi\sigma_y\sigma_z) \\ &= \frac{(1337.786)(11.7)(0.1166)}{(62.5)(100)} \\ &= 0.29 \text{ ppm(v)} \end{aligned}$$

MODEL VALIDATION

To verify the usefulness of the model in predicting workplace exposure concentrations, the model predictions were compared with the limited information obtained in the literature survey. The worker exposure data reported in the literature for DOP ranged from $0.06\text{--}2 \text{ mg/m}^3$ compared with an estimate of 3.77 mg/m^3 from the model for diheptyl phthalate. The literature values were measured during calendering operations not extrusion. For calendering, the off-gassing time would vary because the polymer sheet is usually cooled by chilled rollers not a water trough. The predicted value of 3.77 mg/m^3 represents a worst

case value considering the lack of information on initial concentration, temperature, off-gassing time, and ventilation rates contained in the literature. The literature data on worker exposure to vinyl chloride monomer from extrusion varied from undetectable to 1.3 ppm, compared with the predicted value of 0.29 ppm. The high value of 1.3 ppm represented an area sample not a normal worker breathing zone. The highest exposure measured on a worker was 0.27 ppm. The predicted value was based on an initial concentration of 0.2 weight percent, whereas, no information on the amount of residual monomer was reported in the literature. Most of the measurements of worker exposure in the literature were conducted in 1975 before the amount of residual monomer in polyvinyl chloride was regulated. The value of 0.2 weight percent should result in predicting low values for the maximum concentration when compared with the measurement from 1975. Although the predicted values are similar to the literature values, this comparison neither proves nor disproves the validity of the model.

To validate the model, the worker exposure to different additives must be measured in industrial processing facilities and compared with the model prediction based on accurate measurement of the model variables. If these measurements prove that the model is acceptable, the estimations of the variables could be improved using the information gained in the experiments. These experiments could also show whether future work on correlating the diffusivity to concentration, temperature, and molecular size is necessary. If the model does not predict reasonable worst case values under these controlled circumstances, a new model must be developed. This new model could account for the development of a boundary layer film on the surface of the extrudate instead of using an immediate surface evaporation rate. Another possible model, the shrinking core model, would account for the development of a hardened skin on the surface of the extrudate with an inner core of melted polymer.⁴⁰ The additives would quickly diffuse through the inner core and then slowly diffuse through the outer layer into the environment.

REFERENCES

1. Milkov, L.E., M.V. Aldyreva, T.B. Popova, K.A. Lopukhova, Yu.L. Makarenko, L.M. Malyar, and T.K. Shakhova. Health Status of Workers Exposed to Phthalate Plasticizers in the Manufacture of Artificial Leather and Films Based on PVC Resins. *Environ. Health Perspect.*, 3:175-8, 1973.
2. Roberts, D.R. NIOSH-EPA (National Institute for Occupational Safety and Health/Environmental Protection Agency) Interagency Agreement for the Assessment of Human Health Effects from Exposure to Di-2-(ethylhexyl) Phthalate (Summary Report). PB84-182047, U.S. National Institute for Occupational Safety and Health, Cincinnati, Ohio, 1983, 15pp.
3. Nielsen, J., B. Akesson, and S. Skerfving. Phthalate Ester Exposure - Air Levels and Health of Workers Processing Polyvinylchloride. *Am. Ind. Hyg. Assoc. J.*, 46(11):643-647, 1985.
4. Fischbein, A., J.C. Thornton, L. Berube, F. Villa, and I.J. Selikoff. Lead Exposure Reduction in Workers Using Stabilizers in PVC Manufacture: Effects of a New Encapsulated Stabilizer. *Am. Ind. Hyg. Assoc. J.*, 43(9):652-655, 1982.
5. Karstadt, M. PVC: Health Implications and Production Trends. *Environ. Health Perspect.*, 17:107-115, 1976.
6. Froneberg, B., P.L. Johnson, and P.J. Landrigan. Respiratory Illness Caused by Overheating of Polyvinyl Chloride. *British Journal of Ind. Med.*, 39:239-243, 1982.
7. Jones, J.H. Worker Exposure to Vinyl Chloride and Poly(vinyl Chloride). *Environ. Health Perspect.*, 41:129-136, 1981.
8. Jones, J.H. Worker Exposure to Vinyl Chloride in Vinyl Chloride and Polyvinyl Chloride Production and Fabrication. PB83-116053, U.S. National Institute for Occupational Safety and Health, Cincinnati, Ohio, 1977, 196 pp.

9. Barnhart, W.L., C.R. Toney, and J.B. Devlin. Environmental/Industrial Hygiene Surveys of Vinyl Chloride Monomer Manufacturing Operations and Operations Where Polyvinyl Chloride and Copolymers of Polyvinyl Chloride are Processed. PB82-109976, U.S. National Institute for Occupational Safety and Health, Cincinnati, Ohio, 1975, 110 pp.
10. Bellenger, V., L.B. Carette, E. Fontaine, and J. Verdu. A Possible Mechanism for Benzene Formation During the Pyrolysis of Poly(vinyl chloride). *Eur. Polym. J.*, 18:337-340, 1982.
11. Chang, E.P. and R. Salovey. Pyrolysis of Poly(vinyl Chloride). *J. Polym. Sci., Polym. Chem. Ed.*, 12(12):2927-2941, 1974.
12. Leisztner, L., S. Gal, J. Szanto, and L. Kovacs. Influence of the Morphology of Samples in the Pyrolysis of PVC. *J. Therm. Anal.*, 13:141-147, 1978.
13. Edgerley, P.G. The Oxidative Pyrolysis of Plastics. *Fire Mater.* 4(2):77-82, 1980.
14. Pidduck, A.J. Mass Spectrometric Analysis of Halogenated Polymers. *J. Anal. Appl. Pyrolysis*, 7:215-229, 1985.
15. Israel, S.C., W.C. Yang, and M. Bechard. Characterization of Polymers by Direct Pyrolysis/Chemical Ionization Mass Spectrometry. *J. Macromol. Sci. Chem.*, A22(5-7):779-801, 1985.
16. Kokosa, J.M. and D.J. Doyle, Condensed Phase Pyrolysates Produced by CO₂ Laser Processing of Polymers I: Polycyclic Aromatic Hydrocarbons Obtained from Polyvinyl Chloride. *Polym. Prepr.*, 26(2):255-256, 1985.
17. Liao, J.C. and R.F. Browner. Determination of Polynuclear Aromatic Hydrocarbons in Poly(vinyl chloride) Smoke Particulates by High Pressure Liquid Chromatography and Gas Chromatography-Mass Spectrometry. *Anal. Chem.*, 50(12):1683-1686, 1978.
18. Pausch, J.B., R.P. Lattimer, and H.L.C. Meuzelaar. A New Look at Direct Compound Analysis Using Pyrolysis Mass Spectrometry. *Rubber Chem. Technol.*, 56:1031-1044, 1983.
19. Lattimer, R.P., J.B. Pausch, and H.L.C. Meuzelaar. Pyrolysis Studies of Chlorinated Poly(vinyl chloride). *Macromolecules*, 16:1896-1900, 1983.

20. Kroenke, W.J. and R.P. Lattimer. The Effects of a Synergistic Molybdenum - Copper Smoke Retarder Additive During the Pyrolysis and Combustion of Rigid Poly(vinyl chloride) Compounds. *J. Appl. Polym. Sci.*, 32:3737-3747, 1986.
21. Suzuki, M., S. Tsuge, and T. Takeuchi. Study of the Effect of Stabilizer on the Degradation of Poly(vinyl Chloride) by Pyrolysis-Gas Chromatography. *J. Polym. Sci.*, Part A-1, 10:1051-1060, 1972.
22. Matthews, G. and G.S. Plemper. Effects of Fillers on and the Role of Hydrogen Chloride in the Behavior of PVC in Fires. *Br. Polym. J.*, 16(1):34-38, 1984.
23. Israel, S.C., M.J. Bechard, and M. Abbot. Polymer Characterization by Direct Pyrolysis/Chemical Ionization Mass Spectrometry. *Polym. Prepr.*, 24(1):159-160, 1983.
24. Lum, R.M. Antimony oxide-PVC Synergism: Laser Pyrolysis Studies of the Interaction Mechanism. *J. Polym. Sci., Polym. Chem. Ed.*, 15:489-497, 1977.
25. Tsunoda, R. The Volatilization of Cadmium from Polyvinyl Chloride-Cadmium Mixtures on Heating. *Bull. Chem. Soc. Jpn.*, 48(10):2999-3000, 1975.
26. Pasternak, M., B.T. Zinn, R.O. Gardner, and R.F. Browner. Constituents and Polymer Additives on Oxidative Pyrolysis of Chlorinated Polymers. *Combust. Flame*, 55(1):117-120, 1984.
27. Bove, J.L. and P. Dalven. Pyrolysis of Phthalic Acid Esters: Their Fate. *Sci. Total Environ.*, 36:313-318, 1984.
28. O'Mara, M.M. High-Temperature Pyrolysis of Poly(vinyl chloride): Gas Chromatographic-Mass Spectrometric Analysis of the Pyrolysis Products from PVC Resin and Plastics. *J. Polym. Sci.*, Part A-1, 8:1887-1899, 1970.
29. Crank, J. The Mathematics of Diffusion. Oxford University Press, London, 1956.
30. Vrentas, J.S. and J.L. Duda. Molecular Diffusion in Polymer Solutions. *AIChE J.*, 25(1):1-24, 1979.
31. Biesenberger, J.A., ed., Devolatilization of Polymers. Fundamentals-Equipment-Applications. Hanser Publications, New York, NY, 1983, 97-118.

32. Taverdet, J.L. and J.M. Vergnaud. Study of Transfer Process of Liquid Into and Plasticizer Out of Plasticized PVC by Using Short Tests. *J. Appl. Polym. Sci.*, 29:3391-3400, 1984.
33. El-Hibri, M.J. and D.R. Paul. Effects of Uniaxial Drawing and Heat-Treatment on Gas Sorption and Transport in PVC. *J. Appl. Polym. Sci.*, 30:3649-3678, 1985.
34. Sears, J.K. and J.R. Darby. *The Technology of Plasticizers*. John Wiley & Sons, New York, NY, 1982.
35. Welty, J.R., C.E. Wicks, and R.E. Wilson. *Fundamentals of Momentum, Heat, and Mass Transfer*. John Wiley & Sons, New York, NY, 1979, 495 pp.
36. Wilke, C.R. and P. Chang. Correlation of Diffusion Coefficients in Dilute Solutions. *A.I.Ch.E J.*, 1(2):264-270, 1955.
37. Iammartino, N.R. PVC Makers Move to Mop Up Monomer Emissions. *Chem. Eng.*, 82(25):25-27, 1975.
38. Schroy, J.M. Prediction of Workplace Contaminant Levels. In: *Symposium Proceedings of Control Technology in the Plastics and Resins Industry*, National Institute for Occupational Safety and Health, Cincinnati, Ohio, 1981, pp 190-206.
39. Levenspiel, O. *Chemical Reaction Engineering*, 2nd ed. John Wiley & Sons, New York, NY 1972, pp. 360-368.

BIBLIOGRAPHY

- Barber, R.M. Diffusion In and Through Solids. University Press, Cambridge, 1941.
- Beliczky, L.S. How to Control Worker Exposure to Vinyl Chloride. Int. J. Occup. Health Saf., 44(2):22-25, 1975.
- Bird, R.B., W.E. Stewart, and E.N. Lightfoot. Transport Phenomena. John Wiley & Sons, New York, 1960.
- Crank, J. and G.S. Parks. eds. Diffusion in Polymers, Academic Press, London, 1968.
- Edelson, D., R.M. Lum, W.D. Reents, Jr., W.H. Starnes, Jr., and L.D. Wescott, Jr. New Insights Into the Flame-Retardance Chemistry of Poly(Vinyl Chlorides). Symp. (Int.) Combust., 19:807-14, 1982.
- Gideon, J.A. Engineering Control Technology in Polyvinyl Chloride Polymerization Plants. J. Environ. Pathol. Toxicol., 2(5):285-318, 1979.
- Huggett, C. and B.C. Levin. Toxicity of the Pyrolysis and Combustion Products of Poly(vinyl Chloride): A Literature Assessment. PB86-201621, Consumer Products Safety Commission, Bethesda, MD, 1986, 43 pp.
- Lattimer, R.P., W.J. Kroenke, and R.G. Getts. Effects of Copper and Molybdenum Oxides on the Pyrolysis of Model Compounds of Poly (vinyl Chloride). J. Appl. Polym. Sci., 29(12):3783-94, 1984.
- Lenz, R.W. and R.S. Stein, eds. Structure of Properties of Polymer Films, Plenum Press, New York, 1973.
- Mark, H.F. and N.M. Bikales, eds. Encyclopedia of Polymer Science and Engineering. John Wiley & Sons, New York, 1977.
- Mark, H.F., N.M. Bikales, C.G. Overberger, G. Menges, and J.I. Kroschwitz, eds. Encyclopedia of Polymer Science and Engineering. John Wiley & Sons, New York, 1988.
- Tadmar, Z. and C.G. Gogos. Principles of Polymer Processing. John Wiley & Sons, New York, 1979.

APPENDIX A: REVIEW OF POLYMER PROCESSING TECHNIQUES

BLOW MOLDING

Blow molding is a polymer processing technique to produce hollow objects. A molten hollow tube, called a parison, is clamped in a mold where air or nitrogen is blown into the parison expanding the walls of the tube into the shape of the mold. The cold mold walls solidify the object which is then ejected from the mold.

There are two major types of blow molding processes: injection blow molding and extrusion blow molding. In injection blow molding, the molten polymer is injected into a mold containing a steel rod. The test tube shaped parison is transferred on the steel rod to the air blowing station. Stretching the parison axially before expansion produces biaxial orientation which improves stiffness and impermeability.

In continuous extrusion blow molding, the parison is formed at the same rate as the article is molded, cooled, and ejected. The mold clamps the parison and transfers it to the blowing station. Continuous extrusion blow molding is used for polyvinyl chloride because the slow uninterrupted process reduces hot spots which may degrade the PVC. In intermittent extrusion blow molding, reciprocating screw and ram extruders accumulate a charge of polymer and then extrude the parison quickly. Blow molding, cooling, and ejection occur under the extrusion head, while a new charge of polymer is building up in the extruder.

CALENDERING

Calendering produces a film or sheet by extruding molten polymer between successive pairs of corotating rollers. The most common configuration for a four roll calender is the inverted "L" shape (see Figure A-1). The polymer melt is extruded through the first two rollers forming a sheet which passes over and between the remaining rolls. Difference in temperature, roll speed, and surface finish are used to transfer the sheet between rolls. A high speed "strip" roll takes the sheet off the calender and may stretch the film. To provide a surface finish, a pair of embossing rolls may follow the calender. A series of chilled rollers cool the sheet before it is collected on a wind-up unit. Calendering is used to produce plasticized and rigid PVC sheet and film, because the polymer is exposed to high temperatures for



Figure A-1. Inverted L shape

only a short time. Calendering is commonly used to produce high melt viscosity thermoplastic sheet because of the high production rates and the low mechanical energy input compared to extrusion.

COMPOUNDING

Compounding is the process of mixing additives into the polymer. The additives include plasticizers, heat and light stabilizers, impact modifiers, inert fillers, lubricants, fungicides, antioxidants, and colorants. If the additives are solid particulates, the additives are dispersed in the polymer using a nonintensive mixer, such as a drum tumbler, a double cone blender, a V blender, or a ribbon blender. These batch mixers use tumble blending to mix the additives into the polymer. Spray nozzles may be used to spray liquid additives into the tumbling powder. The ribbon blender, the most common batch mixer, consists of a cylindrical shell in which two spiral ribbons are mounted on a drive shaft. The rotation of the ribbon mixes the additives into the polymer.

If a more intensive mixing is necessary, medium intensity mixers which contain mixing shafts are used. The essential features of these batch mixers are twin shafts with overlapping mixing plows. Intensive-fluxing mixers include the Banbury mixer, single screw extruders, and twin screw extruders. The Banbury mixer consists of two spiral lobed rotors which counterrotate in a figure-eight shaped chamber. The ingredients are fed through a top chute and pushed into the chamber with a ram. The motion of the rotors melts the polymer, and additional cooling may be required to remove excess heat. In single screw extruders, the mixing is not very intensive, so mixing sections are added where the polymer is forced through a narrow gap. Kneaders are single screw extruders which include the rotation of the screw with a reciprocating axial movement. The intensity of mixing can also be improved by using corotating and counterrotating twin screw extruders which have tighter clearances.

COMPRESSION AND TRANSFER MOLDING

Compression and transfer molding are the two main methods of molding parts from thermosetting polymers, although the process can be used for thermoplastics. For example, rigid PVC is compression molded to make phonograph records. In compression or transfer molding, the thermosetting compound is heated to soften it sufficiently to flow into the mold. The fluid is held under pressure until the material polymerizes or crosslinks.

In compression molding, the thermosetting material is placed in the bottom half of an open mold mounted on a press. The press closes resulting in a squeezing flow of the polymer to fill the mold. Heat conducted through the mold walls causes polymerization. Once the part solidifies, it is ejected from the mold. In cold molding, a variation of compression molding, the compound is compacted in a mold at room temperature and then cured in an oven to crosslink the polymer.

In transfer molding, the mold is closed and placed in an open press. The polymer is charged to an open pot at the top of the mold. The press pushes on a plunger placed in the pot forcing the polymer in the pot to flow through a series of gates into the closed mold.

EXTRUSION

Extrusion is a process where a continuous stream of polymer melt is forced through a shaping die. Extrusion is used in both compounding and fabrication stages. Most plastics extruders in the United States are of the single screw variety. Single screw extruders utilize a rotating screw in a cylindrical barrel with a hopper at the feed end and a shaping die at the discharge end. Solid pellets of polymer are gravity fed from the hopper into the solids conveying zone of the screw. The polymer is melted by the shearing action and the heated barrel in the melting zone. The melted polymer is pressurized and forced through the extruder die in the pumping or pressurization zone. A devolatilization section to remove volatiles from the extrudate may follow the first pumping section and be followed by a final pumping section leading to the die. The typical screw has a deep feed section followed by a tapered transition section leading to a shallow, constant depth, pumping section. The screw design determines the quality of mixing and pumping. The diameter length and rotational speed of the screw determine the throughput, residence time, and available heat transfer surface. The extruder is followed by downstream equipment including sizing equipment, cooling system, and cutting or winding equipment.

Twin screw extruders are more expensive, but are used for viscous polymers with limited heat stability, particularly rigid PVC formulations, difficult compounding applications, and

products that require devolatilization sections. Twin screw extruders have two parallel, usually conical, screws mounted in a figure-eight shaped barrel. The screws can be intermeshing or nonintermeshing and rotated in the same or opposite directions. Nonintermeshing, counterrotating extruders are used to mix glass fibers in the polymers melt and for compounding of formulations that require removal of a large amount of volatiles. Intermeshing, counterrotating extruders are used to make PVC pipe and other rigid PVC products at low temperatures and lower stabilizer concentrations. Intermeshing, corotating extruders have a devolatilization section to remove volatile components from the extrudate.

INJECTION MOLDING

Injection molding is a process to produce identical articles from a hollow mold at high production rates. The injection molding equipment consists of an injection unit and a clamping unit. The injection unit melts the polymer and injects it into the mold. The clamping unit opens and closes the mold automatically and ejects the finished product.

The reciprocating screw injection molding unit has replaced the traditional ram injection molding unit. When the screw rotates, it melts and pumps the polymer; when the screw moves forward, it injects the polymer into the mold. The injection molding cycle starts as the screw moves forward, fills the mold with melt, and maintains the pressure. The gate to the mold freezes isolating the mold. After the gate freezes, the screw rotation begins again as the screw moves backward, accumulating polymer in front of the retreating screw. After sufficient polymer melt has accumulated for the next shot, the screw stops. The polymer in the mold has cooled by this time and is ejected from the mold. The mold closes and the cycle begins again.

Sample: HEAT CAPACITY ON PPR-T2-1
Size: 4.4000 mg
Method: HEAT CAPACITY MEASUREMENT
Comment: POLYMER CONTRACT NO. 01-1236-181

DSC
File: A: T2-1-N2.53
Operator: VDB
Run Date: 08/27/87 08:21
D. A. TRUJILLO

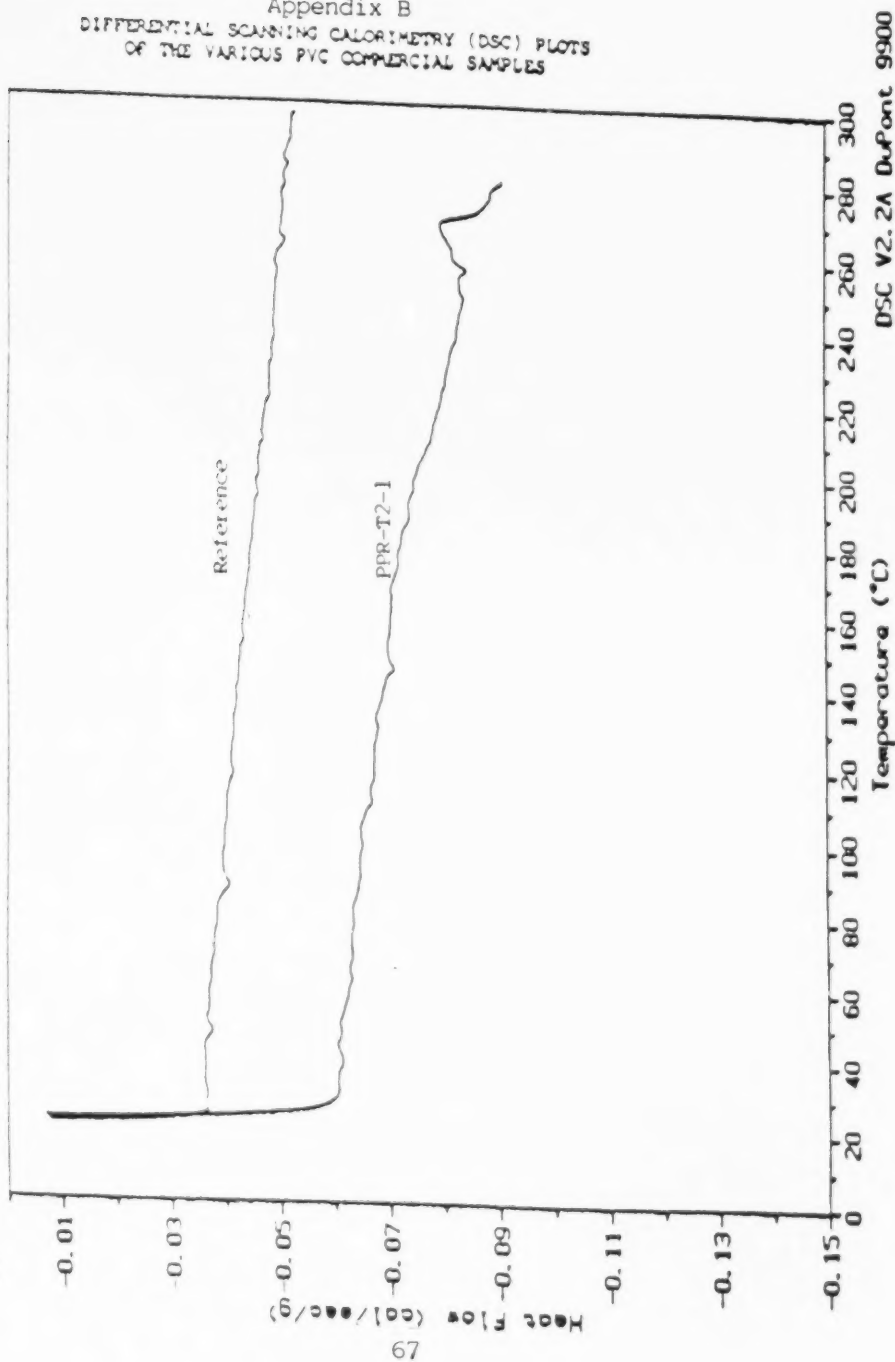


Figure B-1. DSC trace for sample PPR-T2-1, in air at 10°C/min

Sample: HEAT CAPACITY ON PPR-T2-2
Size: 4.6000 mg
Method: HEAT CAPACITY MEASUREMENT
Comment: POLYMER CONTRACT NO. 01-1236-181

DSC

File: A1T2-2-N2.56
Operator: VDB
Run Date: 08/27/87 10:06
D. A. TRUJILLO

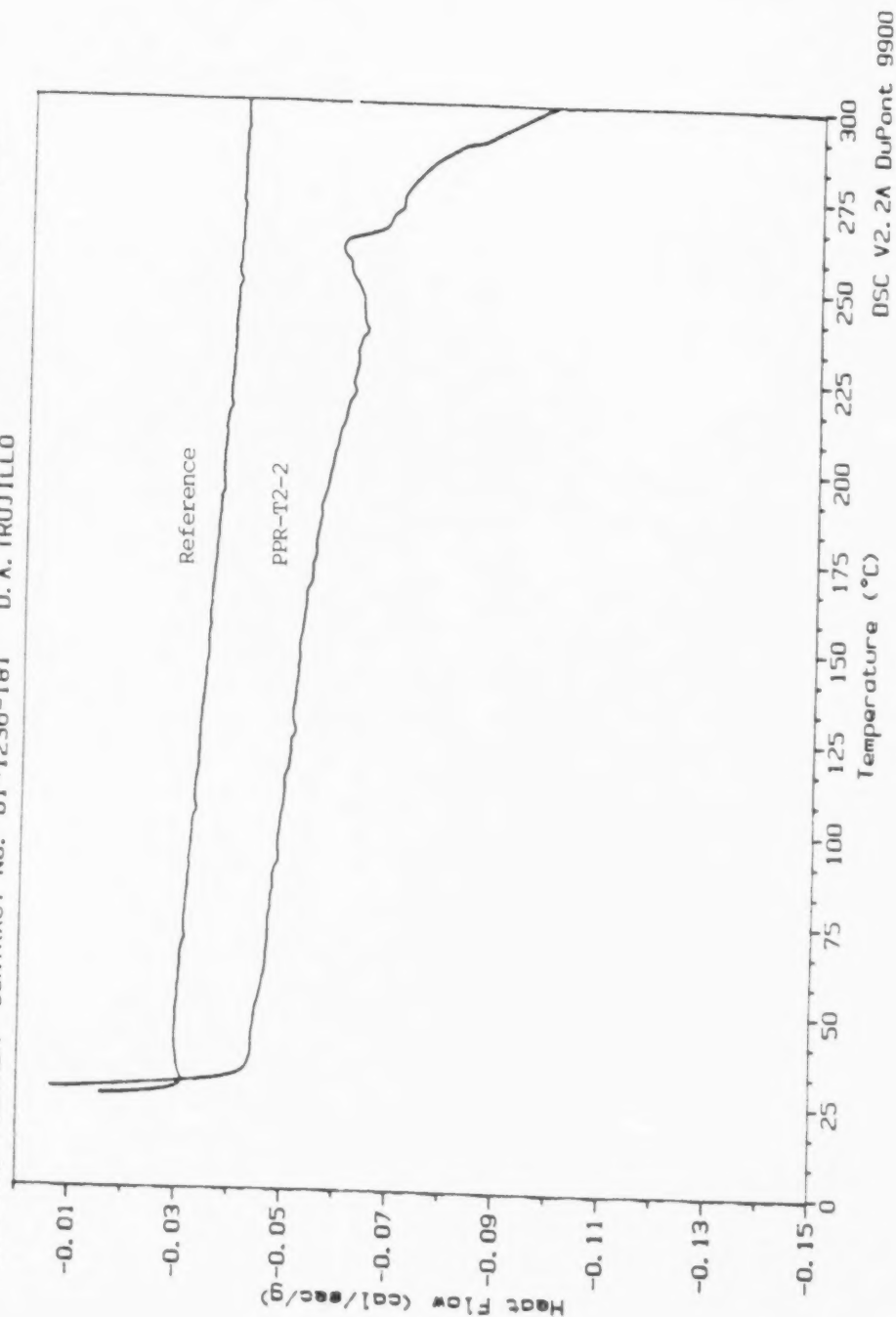


Figure B-2. DSC trace for sample PPR-T2-2, in air at 10°C/min

Sample: HEAT CAPACITY ON PPR-T2-3
Size: 4.7000 mg
Method: HEAT CAPACITY MEASUREMENT
Comment: POLYMER CONTRACT NO. 01-1236-181 D. A. TRUJILLO

DSC

File: A1T2-3-N2.58
Operator: VDB
Run Date: 08/27/87 12:42

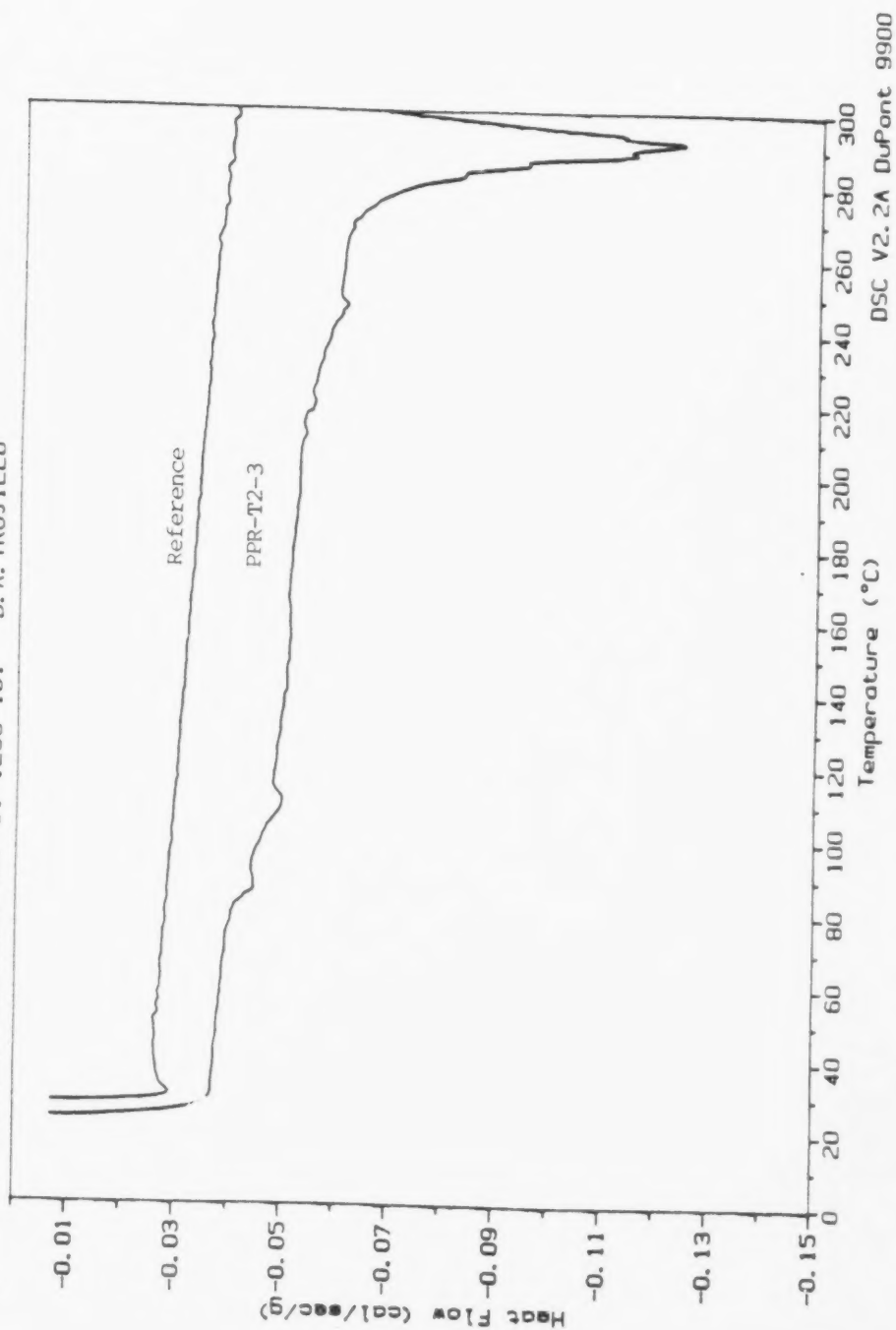


Figure B-3. DSC trace for sample PPR-T2-3, in air at 10°C/min

Sample: HEAT CAPACITY ON PPR-T2-6
Size: 4.7000 mg
Method: HEAT CAPACITY MEASUREMENT
Comment: POLYMER CONTRACT NO. 01-1236-181

DSC

File: A, T2-6-N2.69
Operator: VDB
Run Date: 08/28/87 14.59
D.A. TRUJILLO

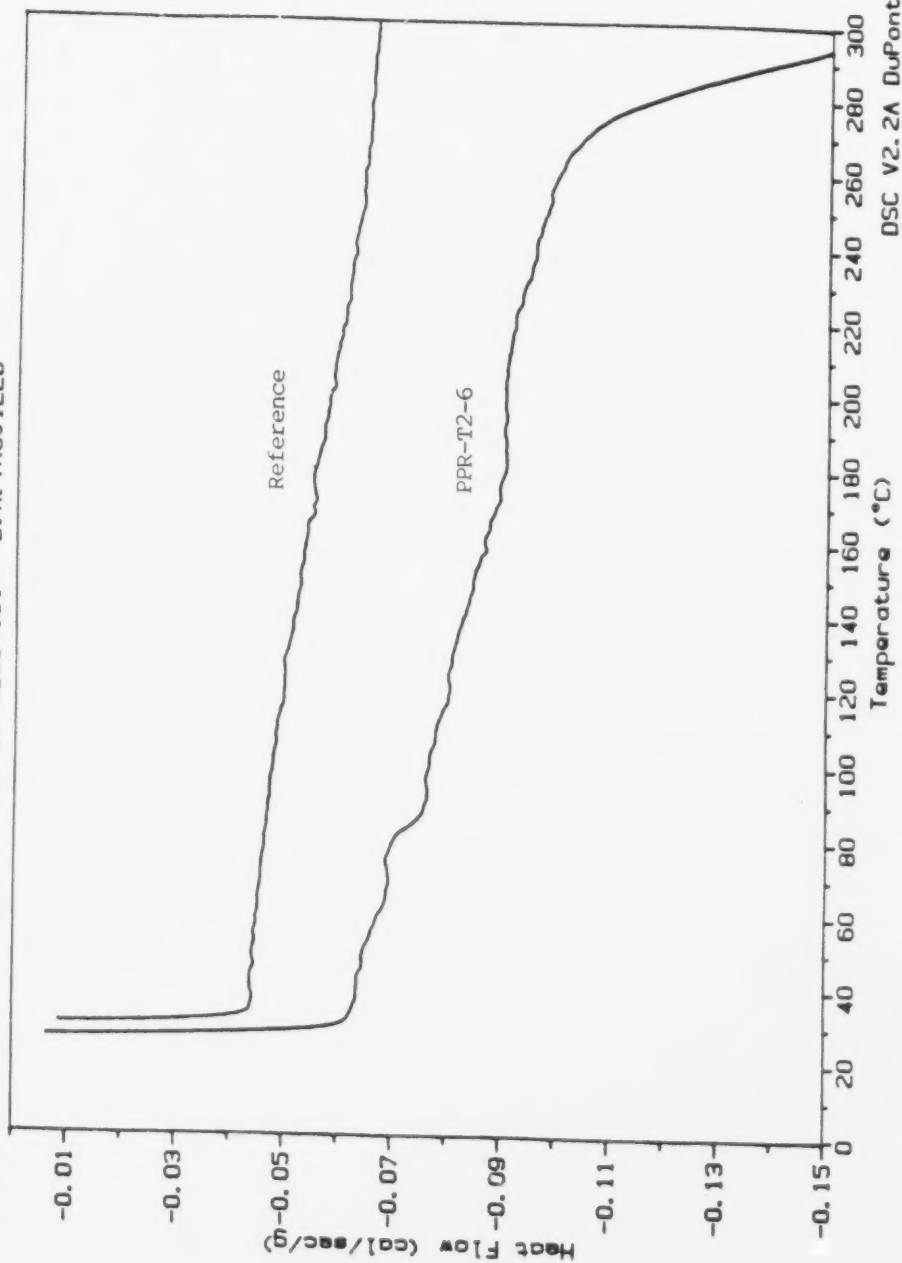


Figure B-4. DSC trace for sample PPR-T2-6, in air at 10°C/min

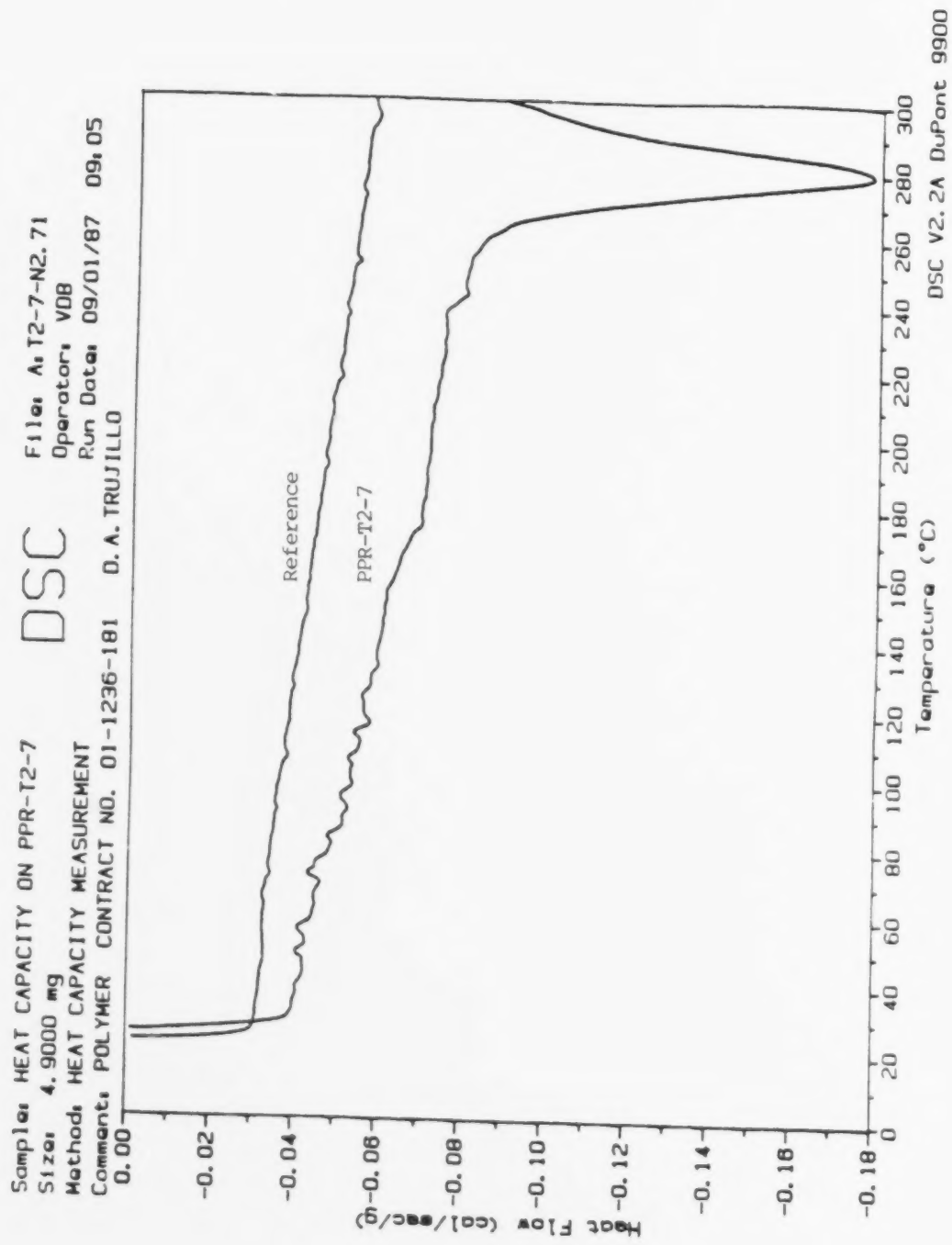


Figure B-5. DSC trace for sample PPR-T2-7, in air at 10°C/min

Appendix C
QUALITY ASSURANCE PROJECT PLAN

for

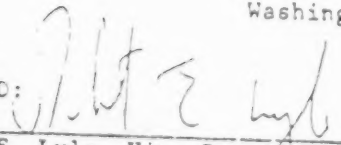
Engineering and Toxic Characterization Studies and Development of
Unit Operations Predictive Models for New Chemicals
Part B: Polymer Processing Research
Task 2. Laboratory Data Study

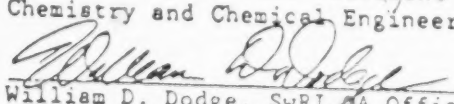
David A. Trujillo
Stuart T. Schwab
Herbert G. Wheeler, Jr.
Southwest Research Institute
San Antonio, Texas 78284

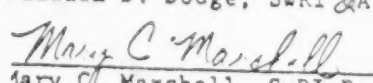
Assistance ID CR813355-01
SwRI Project 01-1236

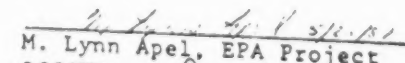
Project Officer
M. Lynn Apel
U.S. Environmental Protection Agency
Office of Toxic Substances
Washington, D.C. 20460

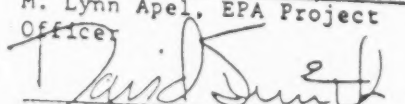
APPROVED:


Robert E. Lyle, Vice President
Chemistry and Chemical Engineering Div


William D. Dodge, SwRI QA Officer


Mary C. Marshall, SwRI Project Manager


M. Lynn Apel, EPA Project
Officer


David Smith, EPA QA Officer

FOREWORD

This document defines the quality assurance procedures which shall be conducted to produce scientifically valid and defensible data of known precision and accuracy. This Quality Assurance Project Plan has been prepared in accordance with the "Interim Guidelines and Specifications for Preparing Quality Assurance Project Plans," QAMS-005/80, December 29, 1980.

Contained are the definitions of project personnel responsibilities; data quality objectives in terms of accuracy and precision; analytical methods to be used; sampling procedures including chain-of-custody requirements; procedures for review of data, use of quality control samples, data acceptance criteria, and provisions for corrective action; and procedures for internal review of the program.

TABLE OF CONTENTS

Foreword

	<u>No. of Pages</u>	<u>Rev</u>	<u>Date</u>
1 Project Description	1	1	3-31-87
2 Project Organization and Responsibility	3	1	3-31-87
3 Quality Assurance Objectives	1	1	3-31-87
4 Sampling Procedures	1	1	3-31-87
5 Sample Custody	1	1	3-31-87
5.1 Sample Identification Labels	1	1	3-31-87
5.2 Proprietary and Confidential Data			
5.3 Bound Logbook Documentation			
6 Calibration Procedures	1	0	1-31-87
7 Analytical Procedures	1	1	3-31-87
8 Data Reduction, Validation and Reporting	2	1	3-31-87
9 Internal Quality Control Checks	1	1	3-31-87
9.1 Replicate Samples			
9.2 Internal Standards			
10 Performance and System Audits	1	1	3-31-87
11 Preventative Maintenance	1	1	3-31-87
12 Routine Procedures to Assess Precision Accuracy, and Completeness	1	1	3-31-87
13 Corrective Action	1	1	3-31-87
14 Quality Assurance Reports to Management	1	1	3-31-87

OFFICIAL DISTRIBUTION:

M. Lynn Apel, EPA Project Officer
 David Smith, EPA QA Officer
 Paul Quillen, EPA Program Office Representative

David A. Trujillo, SwRI Principal Investigator
 William D. Dodge, SwRI QA Officer
 David E. Camann, SwRI QA Coordinator
 Sue R. Durke, SwRI QC Chemist
 Mary C. Marshall, SwRI Project Manager
 Herbert G. Wheeler, SwRI Analytical Coordinator
 Donald J. Mangold, Director, Department of Applied Chemistry
 and Chemical Engineering
 Robert E. Lyle, Vice President, Chemistry and Chemical
 Engineering Division

1.0 PROJECT DESCRIPTION

The Laboratory Data Study objective of the polymer processing research of the cooperative agreement between U.S. Environmental Protection Agency (EPA) and Southwest Research Institute (SwRI) is to analyze emissions from polyvinyl chloride (PVC) samples which contain different additives. The types of off-gassed materials (defined as the emitted volatile and semivolatile gases) may be correlated to the types of additives used in the PVC formulation. Hence, one could predict worker exposures to the hazardous gaseous products resulting from an extrusion process of PVC. The Premanufacture Notices (PMN) review process predicts worker exposure to new polymer additives having comparable physical and chemical properties to those used in this study.

Data will be gathered with a pyrolysis unit interfaced to a tandem gas chromatograph/mass spectrometer. PVC samples, representative of wire cables, pipe, siding, and window frames, will be used. The pyrolysis will be conducted under a helium atmosphere. The volatile materials will be identified by mass spectrometry. Data will be reported as mass of volatile components per sample mass. This study will not take into account the residence time the PVC is exposed to the processing temperature.

The collected data will be used to expand the EPA resources for evaluating exposures and emissions to new additives used in PVC extrusion processing. The data/information gathered for this study will neither be used in the development of EPA regulations nor be used to validate any EPA evaluation procedures.

The following sections of this document present the quality assurance/quality control (QA/QC) activities for this study.

Pyrolysis temperatures will be 150°C, which is close to actual PVC processing temperatures, 300°C, which is the reported temperature for an overheated extruder, and 600°C. These last two temperatures would represent a reasonable "worst case" scenario which assumes nondiffusion limited off-gassing as opposed to bulk extrusion.

2.0 PROJECT ORGANIZATION AND RESPONSIBILITY

The typical duties of the assigned personnel in the organization chart shown in Figure 2.1 are as follows:

SwRI Project Manager

- o monitor study technical progress
- o monitor budget and schedule

SwRI Principal Investigator

- o prepare the work plan
- o supervise project personnel
- o manage finances
- o communicate between EPA and SwRI
- o resolve problems and issues

Analytical Coordinator

- o prepare analytical plan
- o prepare quality assurance project plan for analytical activities
- o develop necessary analytical protocols and standard operating procedures, including control charts
- o train and supervise the analysts
- o check instrument conditions and calibrations
- o monitor control charts
- o review analytical results for questionable data and initiate necessary repeat analyses
- o report problems to the principal investigator and the QC chemist/QA coordinator
- o report analytical and QC data to the sponsor

Sample Acquisitioner

- o obtain commercial samples of PVC
- o log all samples received and transfer to analytical coordinator

Analytical Chemists

- o perform analyses
- o perform analytical calculations
- o perform quality control calculations
- o maintain control charts
- o report problems to the analytical coordinator for resolution

SWRI QA Officer

- o oversee quality assurance activities
- o review all QA Project Plans

QA Coordinator

- o assist the quality assurance project plan preparation
- o supervise the quality control chemist

QC Chemist

- o evaluate protocols
- o review control charts

Effective communications must be maintained among the various project personnel in different locations to develop and implement project activities, to perform specific tasks, and to solve problems. One part of the QA function is to facilitate communications through the establishment of guidelines, the issuance of procedures, and the modification of the guidelines and procedures as circumstances change.

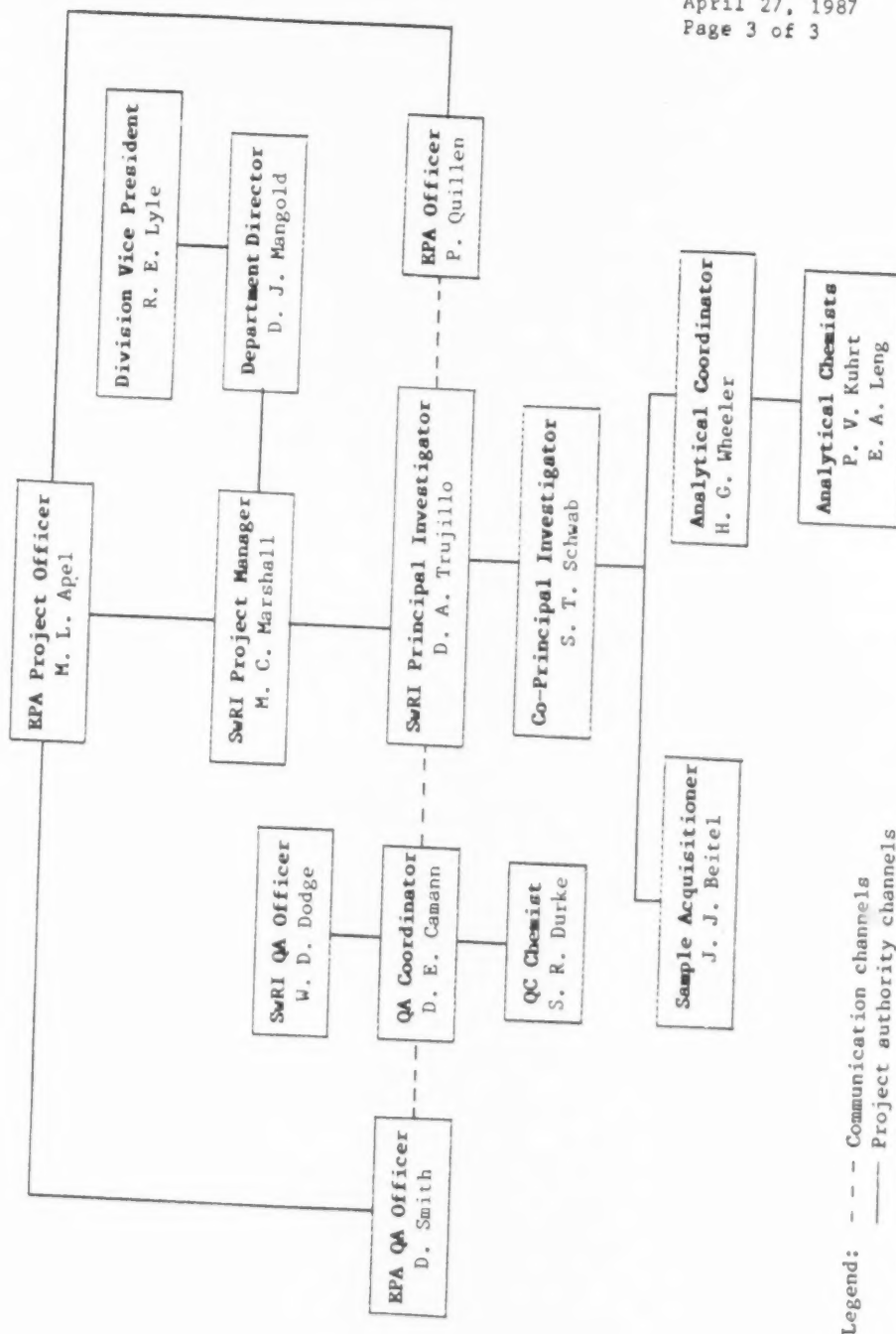


Figure 2-1. Organization Chart

3.0 QUALITY ASSURANCE OBJECTIVES

The research objective is to identify the major off-gassed components from commercially available PVC extrusion-grade resins. SWRI will conduct tandem pyrolysis/gas chromatography/mass spectrometry (Py/GC/MS) on various samples. The major off-gassed components at three temperatures (150°C, 300°C, and 600°C) will be identified and quantitated versus a known internal standard. The detection limits will be determined during the initial experimental activities. The acceptable percentage of precision should fall between 0 and 50%, and the acceptable percentage of accuracy should fall between 50 and 100%. The methods of determining accuracy and precision appear in Section 12.

The off-gassed analytes will be correlated to the various PVC additives which are categorized as follows:

- o plasticizers
- o heat stabilizers
- o processing aids
- o impact modifiers
- o inert fillers
- o light stabilizers
- o fungicides
- o flame retardants
- o antioxidants
- o colorants

It is already known that the pyrolysis of PVC alone produces significant amounts of hydrogen chloride, carbon monoxide, and vinyl chloride monomer. The amounts of other gaseous products will be determined. Only major peaks (i.e., peaks 10 to 20 times the noise level or greater) will be characterized through a mass spectrum library search.

Section 4
Revision 1
April 27, 1987
Page 1 of 1

4.0 SAMPLING PROCEDURES

The samples will be commercially available virgin PVC and extrusion-grade PVC resins in powder and pellet forms. The PVC resins will be pyrolyzed in a Py/GC/MS. The off-gassed material will be swept with helium from the pyrolyzer oven into the gas chromatograph.

5.0 SAMPLE CUSTODY

Polyvinyl chloride (PVC) samples and information on their additives will be obtained from commercial sources.

The guidelines set forth below are intended to maintain the integrity and security of these samples and to document the supplier, condition, and disposition of both samples and their identifying forms.

5.1 Chain-of-Custody Procedures

Samples from various PVC manufacturers and end-product producers will be obtained by Dr. David Trujillo and Mr. Jess Beitel. The samples and corresponding data will be logged in by Dr. Trujillo. The samples will be transferred to Mr. Bert Wheeler for laboratory analysis. Mr. Wheeler will be responsible for sample custody.

5.2 Proprietary and Confidential Data

The PVC sample information will be kept confidential if so requested by the supplier. The data will only be used to help identify the off-gassed products and to identify whether certain additives affect the amount of off-gassed products.

5.3 Bound Logbook Documentation

The amount, condition, and physical aspects of the samples will be recorded upon receipt. The composition of the PVC materials will be recorded when appropriate.

The sample analysis by Py/GC/MS should provide a fingerprint pattern for that particular sample. The conditions for pyrolysis, gas chromatography, and mass spectrometry will be recorded for each sample. The amount of sample used will be recorded in order to estimate the amount of off-gassed material for processing scale.

6.0 CALIBRATION PROCEDURES

Procedures for this project involve: 1) calibrating the GC/MS system to assure correct mass assignment of the spectrometer and 2) calibrating the electro-balance for weighing samples to assure accurate weight data.

The spectrometer mass assignment is calibrated with perfluorotributylamine (FC-43). The assignment is checked and verified by two data system programs. This procedure is performed once daily.

The electro-balance is calibrated according to manufacturer's procedures and verification includes checking the weights of known standards made to Class S specifications of the National Bureau of Standards. This procedure is performed at each setting or at a minimum on a daily basis.

7.0 ANALYTICAL PROCEDURES

SwRI has conducted a number of off-gassing studies to qualitate and/or quantitate constituents in various matrix materials. The temperatures for some extrusion processes were identified to be about 150°C. Therefore, the pyrolysis temperatures SwRI intends to use are 150°C, 300°C and 600°C. The latter values were estimated to be a reasonable "worst case" situation for an overheated extruder. The samples will be pyrolyzed initially under inert atmosphere (helium) and, at a later date, using an air atmosphere to observe oxidation products.

The GC/MS conditions are as follows:

<u>GC</u>	Column	DB-5, 30 m capillary, 0.25 mm ID, fused silica
	Injector Port Temp	250°C
	Column Temp	35°C for 2 min ramp 10°C/min
		295°C
	Flow Rate	1 mL/min
<u>MS</u>	Mass Range	25-525

The analytical protocol for conducting these pyrolysis studies are as follows:

- 1) Calibrate GC/MS system as set forth in Section 6.
- 2) Add 100 ng of internal standard to blank pyrolysis tube.
- 3) Perform pyrolysis/GC/MS system blank run using conditions with which samples are to be analyzed.
- 4) Add 100 ng of internal standard to pyrolysis tube containing preweighed sample.
- 5) Perform analysis under same conditions as 3) above.
- 6) Reweigh sample and record weight.
- 7) Continue analyzing samples; perform blank analysis as necessary.

8.0 DATA REDUCTION, VALIDATION AND REPORTING

Figure 8.1 presents the general flow of data from the initial analysis through its final submission to EPA.

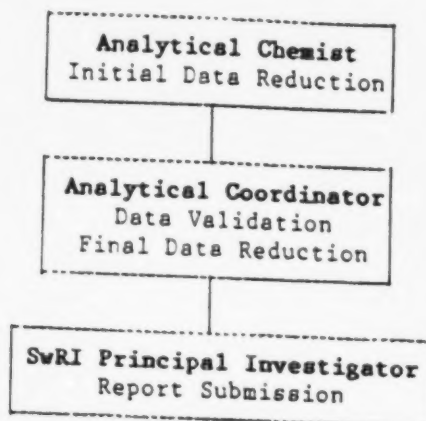


Figure 8.1. Data Reduction and Validation Flow Chart

8.1 Data Reduction

The initial data reduction will be the responsibility of the analyst. Raw data from the quantitative analyses will consist of chromatograms and computer-generated chromatograms supplemented by computer-assisted data calculation. Quantitation of unidentified peaks will be based upon the response to an appropriate internal standard. Values will be determined in micrograms and calculated on a per pound PVC basis.

8.2 Data Validation

The analytical coordinator will perform a review of all data as it is generated. This review will cover the analytical program and examination/verification of results.

a. Review of Analytical Program

The analytical coordinator will review each set of results to ensure that the required program elements, including method blanks and QA samples, have been accomplished according to the program design. The supporting data will be reviewed to ensure that analyses were performed under the correct conditions and that all required procedural steps were performed.

b. Examination and Verification of Results

The analytical coordinator will examine the results obtained, and the pertinent calibration curves to ensure that the results are reasonable and that the analyst has interpreted the results correctly. Any unusual or unexpected results will be reviewed and a resolution will be made as to whether the analysis should be repeated or the result recalculated.

8.3 Reporting

Reports will state the dates of analyses and include an SwRI identification number on the data report form generated by SwRI. The analytical results will be reported on this form and include method blanks, background, QC sample results (if appropriate), and sample results. The appropriate units of measurement will be clearly evident and will be expressed in weight/weight form (e.g., nanograms/milligram, ng/mg).

9.0 INTERNAL QUALITY CONTROL CHECKS

Due to the type of samples that will be used in this study, QC checks will be performed at the discretion of the QA coordinator. Close approximately to the amounts of off-gassed material can be made by comparison against an internal standard of known boiling point. Details of this aspects of the QC checks are provided below.

9.1 Replicate Samples

The minimum number of two replicate samples resulting from any given PVC sample will be analyzed. Thus, any fingerprint pattern generated from any sample can be averaged as to quantity of off-gassed material to sample weight based on identical Py/GC/MS conditions.

9.2 Internal Standards

Samples will be spiked with internal standards of known amounts. This will permit calculations to determine the relative response factors of the off-gassed materials. All components of the off-gassed material will be correlated with sample weight and internal standard response factors. The concentrations of sample components will be calculated by assuming that sample components have similar response factors to those of the internal standards. Since the laboratory work is developmental, there are several unknowns which do not allow absolute quantification of the instrumental response data.

Section 10
Revision 1
April 27, 1987
Page 1 of 1

10.0 PERFORMANCE AND SYSTEM AUDITS

This QA program will include audits of the analysis and data handling at the discretion of the QA coordinator. At the minimum, prior to analysis of actual sample data, the QC chemist will review the analytical protocols prepared by the analytical coordinator and SwRI principal investigator. The purpose of the audits will be to assist in the identification and correction of deficiencies and to ensure that equipment and procedures meet the quality requirements of the project.

11.0 PREVENTATIVE MAINTENANCE

The instrumentation required on this program requires little in the way of regularly scheduled preventative maintenance. Most maintenance must be performed on an as-needed basis when performance begins to degrade as evidenced by poor sensitivity. An example of such maintenance would be the removal and cleaning of the quartz inserts found in the gas chromatograph/pyrolysis interface.

Adequate supplies of spare equipment including quartz inserts, glassware, and other laboratory items are maintained.

12.0 ROUTINE PROCEDURES TO ASSESS PRECISION, ACCURACY AND COMPLETENESS

The instrument will be calibrated with perfluorotributylamine (FC-43) at the start of each workday. One blank will be run at the appropriate temperature (150, 300, or 600°C) prior to sample analysis at that temperature. Samples will be run in duplicate at each temperature.

The precision of the analysis methods will be calculated as the percent difference of the results of the analysis from replicate samples. The equation will be expressed as:

$$\% \text{ Difference} = \left[\frac{\frac{\text{Sample 1 result}}{\text{wt Sample 1}} - \frac{\text{Sample 2 result}}{\text{wt Sample 2}}}{\left(\frac{\text{Sample 1 result}}{\text{wt Sample 1}} + \frac{\text{Sample 2 result}}{\text{wt Sample 2}} \right) / 2} \right] \times 100$$

Data accuracy data will be calculated from the results of the internal standard. The measure of accuracy will be the percent recovery expressed as:

$$\% \text{ Recovery} = \frac{\text{Observed}}{\text{Known}} \times 100$$

The analytical coordinator will calculate the percent values for accuracy and precision; he will promptly report these values to the SwRI principal investigator, SwRI project manager, and QA coordinator. The SwRI principal investigator will include all accuracy and precision data in the quarterly progress and final reports.

Section 13
Revision 1
April 27, 1987
Page 1 of 1

13.0 CORRECTIVE ACTION

Due to the nature of this Laboratory Data Study, control limits will be identified and set for future work in this area. The SwRI principal investigator will recommend control limits for accuracy and precision as well as criteria and responsibilities for corrective action for approval by the SwRI project manager and QA coordinator.

14.0 QUALITY ASSURANCE REPORTS TO MANAGEMENT

The SwRI principal investigator will report accuracy and precision data in the quarterly progress and final reports. When corrective action is needed (see Section 13), the responsible individual will submit a corrective action report to the SwRI principal investigator, SwRI project manager, and QA coordinator, and the report will be included in the QA section of the quarterly progress report.

Assessments of data precision, accuracy, and completeness, and reports of corrective action will be included in the QA section of the final report.

APPENDIX D. GC/MS IDENTIFICATIONS OF OFF-GASSED PRODUCTS
AT 300°C AND 600°C

TABLE D-1. OFF-GASSED PRODUCTS OF SAMPLE PPR-T2-1 AT 300°C

PVC Sample ID: PPR-T2-1
File ID: C07288706
Pyrolysis conditions: 10 SC -- 300C
GC temperature program: 30C // 2min // 10C/min // 295C

Tentative compound ID:	RUN 1		RUN 2	
	Scan #	Amount (ng/mg)	Scan #	Amount (ng/mg)
C-7 ALKENES	220-250	1992	220-250	783
C-7 TO C-9 UNSATURATED HYDROCARBONS	430-470	2814	430-480	1429
UNKNOWN HYDROCARBON	488	272	491	63
MONOCHLORINATED SATURATED HYDROCARBON	520	1017	521	125
C-7 HYDROCARBON	531	1241	532	255
UNSATURATED HYDROCARBONS	657-690	3443	650-690	385
MONOCHLORINATED HYDROCARBON	738	553	737	447
UNKNOWN	743	324	--	96
UNKNOWN	875	171	--	0
MONOCHLORINATED HYDROCARBON	888	309	--	0
UNKNOWN AROMATIC	931	226	929	0
1,2-BENZENE DICARBOXYLIC ACID	--	0	1277	47
DI-HEPTYL PHTHALATE	--	0	1682	149
	Amount Recovered	12362	Amount Recovered	8780
				12434
Initial Sample Weight	Amount (ng)		Amount (ng)	
Wt. Loss	0.60		0.54	
% Recovery	0.32		0.33	
	2.3 %		2.0 %	

TABLE D-2. OFF-GASSED PRODUCTS OF SAMPLE PPR-T2-2 AT 300°C

PVC Sample ID: PPR-T2-2
 File ID: C07288702
 Pyrolysis conditions: 10 SC -- 300C
 GC temperature program: 30C // 2min // 10C/min // 295C

Tentative compound ID:	RUN 1		RUN 2	
	Scan #	Amount (ng/mg)	Scan #	Amount (ng/mg)
UNSATURATED HYDROCARBONS	420-540	304.7	420-540	2707
C-12 BRANCHED ALKANE	581	62	583	45
C-12 ALKANE, BRANCHED	--	0	596	27
UNSATURATED HYDROCARBONS	690-840	2038	700-825	2990
1,2-BENZENEDICARBOXYLIC ACID	878	112	880	305
UNKNOWN AROMATIC	1270	179	1270	174
UNSATURATED HYDROCARBONS	1295-1400	2130	1270-1400	2056
PHthalATES, DIISODECYL	1800-2100	102470	1800-2100	67270
	Amount Recovered	110038	Amount Recovered	75574
Initial Sample Weight	Amount (mg)		Amount (mg)	
Wt. Loss	0.64		0.63	
% Recovery	0.36		0.22	
	19.6 %		21.6 %	

TABLE D-3. OFF-GASSED PRODUCTS OF SAMPLE PPR-T2-3 AT 300°C

PVC Sample ID: PPR-T2-3
 File ID: C07298705
 Pyrolysis conditions: 10 SC -- 300C
 GC temperature program: 30C // 2min // 10C/min // 295C

Tentative compound ID:	RUN 1		RUN 2	
	Scan #	Amount (ng/mg)	Scan #	Amount (ng/mg)
HYDROCHLORIC ACID (DOT)	--	0	228	1007
UNSATURATED HYDROCARBON	--	0	282	51
UNSATURATED HYDROCARBON	--	0	339	39
BENZOIC ACID	--	0	759	116
NAPHTHALENE	765	32	763	49
C-12 BRANCHED ALKENE	776	12	776	15
UNSATURATED HYDROCARBON	820	28	--	0
1,2-BENZENE DICARBOXYLIC ACID	867	28	--	0
UNKNOWN	1056	1038	1058	379
UNKNOWN	--	0	1279	36
Amount Recovered		1138	Amount Recovered	1692
Initial Sample Weight	Amount (mg)		Amount (mg)	
Wt. Loss	0.82		0.94	
% Recovery	0.56		0.44	
	0.2 %		0.4 %	

TABLE D-4. OFF-GASSED PRODUCTS OF SAMPLE PPR-T2-6 AT 300°C

PVC Sample ID: PPR-T2-6
 File ID: C08038705
 Pyrolysis conditions: 10 SC -- 300C
 GC temperature program: 30C // 2min // 10C/min // 295C

Tentative compound ID:	RUN 1		RUN 2		ID
	Scan #	Amount (ng/ng)	Scan #	Amount (ng/ng)	
BRANCHED SATURATED HYDROCARBON	500-700	1737	500-700	1712	1
UNKNOWN	494	121	502	154	24
ALKYL BENZENE	528	238	533	245	3
BENZOIC ACID	741	211	747	359	52
1,2-BENZENEDICARBOXYLIC ACID	873	98	878	149	41
	Amount Recovered	2405	Amount Recovered	2619	
Initial Sample Weight	Amount (ng)		Amount (ng)		
Wt. Loss	1.00		1.00		
% Recovery	0.26		0.38		
	0.9 %		0.7 %		

TABLE D-5. OFF-GASSED PRODUCTS OF SAMPLE PPR-T2-7 AT 300°C

PVC Sample ID: PPR-T2-7
 File ID: C08048703
 Pyrolysis conditions: 10 SC -- 300C
 GC temperature program: 30C // 2min // 10C/min // 295C

Tentative compound ID:	RUN 1		RUN 2		SD
	Scan #	Amount (ng/mg)	Scan #	Amount (ng/mg)	
HYDROCHLORIC ACID (DOT)	--	0	200	3785	200
BENZENE	205	91	--	0	200
UNKNOWN	--	0	211	908	200
3-OCTENE, (E)-	334	1025	334	1899	60
UNKNOWN AROMATIC	501	625	505	383	48
UNKNOWN	586	162	594	386	82
ACETIC ACID, ALKYL ESTER	--	0	711	192	200
BENZOIC ACID	--	0	752	878	200
	Amount Recovered	1903	Amount Recovered	8431	

Initial Sample Weight	Amount (mg)		Amount (mg)		
Wt. Loss	0.80		0.86		
% Recovery	0.42		0.37		
	0.4 %		2.0 %		

TABLE D-6. OFF-GASSED PRODUCTS OF SAMPLE PPR-T2-1 AT 600°C

PVC Sample ID: PPR-T2-1
 File ID: C07288704
 Pyrolysis conditions: 10 SC -- 600C
 GC temperature program: 30C // 2min // 10C/min // 295C

Tentative compound ID:	RUN 1		RUN 2		ΣD
	Scan #	Amount (ng/mg)	Scan #	Amount (ng/mg)	
BENZENE	204	13032	205	9315	33
C-7 UNSATURATED HYDROCARBONS	220-250	6568	220-240	5327	21
METHYL-BENZENE	299	2180	302	1623	29
BENZENE, ETHYL-	--	0	408	237	200
C-9 ALKENES	430-470	11321	440-470	8855	24
UNKNOWN HYDROCARBON	487	1137	489	877	26
ALKYL-BENZENE	--	0	505	134	200
MONOCHLORINATED HYDROCARBON	517	2851	519	2553	11
FORMIC ACID, HEPTYL ESTER	531	6210	--	0	200
UNKNOWN	--	0	534	4586	200
UNKNOWN HYDROCARBON	--	0	554	153	200
ALKYL-BENZENE	--	0	594	244	200
ALKYL-BENZENE	604	542	606	427	24
C10-C11 UNSATURATED HYDROCARBONS	613	1077	616	809	28
UNKNOWN HYDROCARBON	640-701	11078	639-685	8228	30
UNKNOWN	--	0	693	108	200
UNKNOWN AROMATIC	--	0	703	719	200
MONOCHLORINATED HYDROCARBON	725	280	726	202	32
UNKNOWN HYDROCARBON	734	2471	736	2211	11
NAPHTHALENE	743	4219	746	2351	57
UNKNOWN	762	2031	764	2357	15
1-METHYL NAPHTHALENE	--	0	841	129	200
1,2-BENZENE DICARBOXYLIC ACID	868	591	870	439	30
MONOCHLORINATED HYDROCARBON	897	12003	901	13018	8
NAPHTHALENE, 2-ETHENYL-	927	2333	929	2048	13
UNKNOWN PNA	945	1676	946	1148	37
BENZOIC ACID, ALKYL-ESTER	1119	251	1120	178	34
UNKNOWN AROMATIC	1183	174	1184	162	7
UNKNOWN AROMATIC	--	0	1211	191	200
BENZOIC ACID, HEXYL ESTER	1275	292	1275	582	66
UNKNOWN HYDROCARBON	1329	224	1330	192	15
UNKNOWN HYDROCARBON	1382	338	1382	256	28
PHthalATES, DIHEPTYL-	1462	207	1462	215	4
	1600-2000	307566	1600-2000	336462	9
Amount Recovered		390652	Amount Recovered	406336	
	Amount (mg)		Amount (mg)		
Initial Sample Weight	0.45		0.50		
Wt. Loss	0.24		0.34		
% Recovery	73.2 %		59.2 %		

TABLE D-7. OFF-GASSED PRODUCTS OF SAMPLE PPR-T2-2 AT 600°C

PVC Sample ID: PPR-T2-2
 File ID: C07278702
 Pyrolysis conditions: 10 SC -- 600C
 GC temperature program: 30C // 2min // 10C/min // 295C

Tentative compound ID:	RUN 1		RUN 2		A
	Scan #	Amount (ng/mg)	Scan #	Amount (ng/mg)	
BENZENE	208	8362	208	2424	110
BENZENE, METHYL-	310	1680	310	1475	13
UNSATURATED HYDROCARBONS	440-560	23209	450-560	20944	10
BENZENE, ETHYL-	--	0	449	1056	200
C-10 BRANCHED ALKENE	571	463	562	391	17
ALKYL BENZENE	628	921	--	0	200
UNSATURATED HYDROCARBON	--	0	697	158	200
UNSATURATED HYDROCARBONS	700-870	32845	700-835	19788	50
NAPHTHALENE	775	1924	761	1402	31
NAPHTHALENE, 1-METHYL-	882	506	866	369	31
1,2-BENZENEDICARBOXYLIC ACID	912	9646	891	6308	42
2-ETHENYL NAPHTHALENE	957	398	941	328	19
UNKNOWN AROMATIC	--	0	1115	158	200
UNKNOWN AROMATIC	1286	361	1266	125	97
HYDROCARBONS/BENZOIC ACID ESTERS	1300-1450	5391	1280-1440	3817	34
UNKNOWN	--	0	1333	110	200
PHTHALATES, DIISODECYL	1800-2200	833790	1810-2100	93707	160
Amount Recovered		919497	Amount Recovered	152560	
	Amount (mg)		Amount (mg)		
Initial Sample Weight	0.65		0.55		
Wt. Loss	0.33		0.33		
% Recovery	181.1 %		25.4 %		

TABLE D-8. OFF-GASSED PRODUCTS OF SAMPLE PPR-T2-3 AT 600°C

PVC Sample ID: PPR-T2-3
 File ID: C07298704
 Pyrolysis conditions: 10 SC -- 600C
 GC temperature program: 30C // 2min // 10C/min // 295C

Tentative compound ID:	RUN 1		RUN 2		SD
	Scan #	Amount (ng/mg)	Scan #	Amount (ng/mg)	
BENZENE	208	19501	204	20196	4
C-7 BRANCHED ALKENE	284	199	--	0	200
BENZENE, METHYL	306	1726	301	2467	35
BENZENE, ETHYL	413	197	406	378	63
BENZENE, 1,2-DIMETHYL	449	466	415	143	106
BENZENE, DIMETHYL	--	0	442	917	200
BENZENE, 1-ETHENYL-2-METHYL	509	93	503	164	55
BENZENE, PROPYL	518	155	512	255	49
UNKNOWN	539	197	532	189	4
BENZENE, 1-ETHYL-3-METHYL	548	86	541	187	74
BENZENE, ALKYL	565	166	--	0	200
UNKNOWN	--	0	579	279	200
BRANCHED ALKENE	585	399	--	0	200
BRANCHED ALKENE	594	152	--	0	200
BENZENE, 1-ETHENYL-2-METHYL	598	151	592	427	96
UNKNOWN CHLORINATED	602	75	--	0	200
BENZENE, 1-ETHENYL-2-METHYL	610	301	604	415	32
BENZENE, 1-PROPENYL	--	0	613	511	200
BENZENE, 1-ETHENYL-4-METHYL	619	339	--	0	200
BENZENE, BUTYL	630	57	--	0	200
BENZENE, (1-METHYL-1-PROPENYL)-,...	--	0	724	122	200
ALKYL BENZENE	--	0	729	225	200
ALKYL BENZENE	--	0	740	503	200
UNKNOWN	744	351	--	0	200
NAPHTHALENE	769	3678	763	4488	20
NAPHTHALENE, 1-METHYL	873	344	868	667	64
1,2-BENZENEDICARBOXYLIC ACID	892	1424	--	0	200
UNKNOWN	899	202	--	0	200
2-ETHENYL NAPHTHALENE	949	797	--	0	200
NAPHTHALENE, 1-(2-PROPENYL)	966	218	--	0	200
UNKNOWN	1057	2668	--	0	200
UNKNOWN AROMATIC	1124	199	--	0	200
BENZENE, ALKYL	1216	118	--	0	200
PHENANTHRENE	1275	429	--	0	200
Amount Recovered		34689	Amount Recovered	32533	
		Amount (mg)			Amount (mg)
Initial Sample Weight		0.84			0.72
Wt. Loss		0.62			0.54
% Recovery		4.7 %			4.3 %

TABLE D-9. OFF-GASSED PRODUCTS OF SAMPLE PPR-T2-6 AT 600°C

PVC Sample ID: PPR-T2-6
 File ID: C08038703
 Pyrolysis conditions: 10 SC -- 600C
 GC temperature program: 30C // 2min // 10C/min // 295C

Tentative compound ID:	RUN 1		RUN 2		XD
	Scan #	Amount (ng/mg)	Scan #	Amount (ng/mg)	
BENZENE	204	17690	207	17244	3
2-PROPENOIC ACID, 2-METHYL-, METHYL ESTER	244	746	248	780	4
BENZENE, METHYL-	298	1914	301	6415	108
BENZENE, ETHYL-	404	244	405	370	41
ALKYL-BENZENE	437	688	442	789	14
BRANCHED SATURATED HYDROCARBONS	500-700	4911	500-700	3290	40
ALKYL-BENZENE	510	338	511	171	66
ALKYL-BENZENE	539	567	541	296	63
ALKYL-BENZENE	--	0	591	297	200
ALKYL-BENZENE	602	391	603	346	12
ALKYL-BENZENE	611	418	613	396	5
C3-C4 ALKYL BENZENE	738	326	738	313	4
NAPHTHALENE	761	2727	763	2923	7
BENZOIC ACID	788	1449	794	1550	7
NAPHTHALENE, 1-METHYL-	866	359	868	542	41
1,2-BENZENEDICARBOXYLIC ACID	888	2374	891	1332	56
2-ETHENYL NAPHTHALENE	942	565	--	0	200
Amount Recovered		14425	Amount Recovered	11456	
		Amount (mg)			Amount (mg)
Initial Sample Weight		0.98			1.00
Wt. Loss		0.66			0.76
% Recovery		5.3 %			4.9 %

TABLE D-10. OFF-GASSED PRODUCTS OF SAMPLE PPR-T2-7 AT 600°C

PVC Sample ID: PPR-T2-7
 File ID: C08048701
 Pyrolysis conditions: 10 SC -- 600C
 GC temperature program: 30C // 2min // 10C/min // 295C

Tentative compound ID:	RUN 1		RUN 2		ΣD
	Scan #	Amount (ng/mg)	Scan #	Amount (ng/mg)	
BENZENE	201	14913	200	21003	34
2-PROPENOIC ACID, 2-METHYL-, METHYL ESTER	240	4198	240	10508	86
METHYL BENZENE	294	1603	292	2611	48
3-OCTENE, (E)-	328	2476	326	1110	76
HYDROCHLORIC ACID (DOT)	--	0	342	5513	200
2-PROPENOIC ACID, 1-METHYLPROPYL ESTER	434	1260	--	0	200
BENZENE, ETHYL-	--	0	431	1675	200
UNKNOWN AROMATIC	498	1637	--	0	200
BRANCHED ALKANE	--	0	499	686	200
UNKNOWN	--	0	534	1671	200
ALKYL BENZENE	581	218	580	1076	133
ALKYL BENZENE	603	215	601	499	79
NAPHTHALENE	751	1899	750	3107	48
BENZOIC ACID	--	0	777	1787	200
NAPHTHALENE, 1-METHYL-	857	193	857	534	94
NAPHTHALENE, 1-METHYL-	874	283	873	570	67
2-ETHENYL NAPHTHALENE	933	200	933	491	84
Amount Recovered		29097	Amount Recovered	52841	
		Amount (mg)			Amount (mg)
Initial Sample Weight		0.89			0.71
Wt. Loss		0.64			0.49
% Recovery		4.1 %			7.7 %

APPENDIX E. LOTUS SPREADSHEET CALCULATIONS

	Case 1	Case 2	Case 3
Datf/L ²	0	1.0E-10	1.0E-09
SUM	1.233	1.233	1.233
1-8*SUM/Pi ²	0.000	0.000	0.000
Log(G/wAom)			
Log(Datf/L ²)		-10	-9

INDIVIDUAL EXPONENTIAL TERMS			
m	Case 1	Case 2	Case 3
0	1.0000000	1.0000000	1.0000000
1	0.1111111	0.1111111	0.1111111
2	0.0400000	0.0400000	0.0400000
3	0.0204082	0.0204082	0.0204082
4	0.0123457	0.0123457	0.0123457
5	0.0082645	0.0082645	0.0082645
6	0.0059172	0.0059172	0.0059171
7	0.0044444	0.0044444	0.0044444
8	0.0034602	0.0034602	0.0034602
9	0.0027701	0.0027701	0.0027701
10	0.0022676	0.0022676	0.0022676
20	0.0005949	0.0005949	0.0005949
30	0.0002687	0.0002687	0.0002687
40	0.0001524	0.0001524	0.0001524
50	0.0000980	0.0000980	0.0000980
100	0.0000248	0.0000248	0.0000247
150	0.0000110	0.0000110	0.0000110
200	0.0000062	0.0000062	0.0000062
250	0.0000040	0.0000040	0.0000040
300	0.0000028	0.0000028	0.0000028
350	0.0000020	0.0000020	0.0000020
400	0.0000016	0.0000016	0.0000015
450	0.0000012	0.0000012	0.0000012
500	0.0000010	0.0000010	0.0000010
550	0.0000008	0.0000008	0.0000008
600	0.0000007	0.0000007	0.0000007
650	0.0000006	0.0000006	0.0000006
700	0.0000005	0.0000005	0.0000005
750	0.0000004	0.0000004	0.0000004
800	0.0000004	0.0000004	0.0000004
850	0.0000003	0.0000003	0.0000003
900	0.0000003	0.0000003	0.0000003
950	0.0000003	0.0000003	0.0000003
1000	0.0000002	0.0000002	0.0000002

	Case 4	Case 5	Case 6
DAtf/L ²	1.0E-08	1.0E-07	1.0E-06
SUM	1.233	1.233	1.231
1-8*SUM/Pi ²	0.000	0.001	0.002
Log(G/wAOm)		-3.0	-2.7
Log(DAtf/L ²)	-8.0000	-7	-6

INDIVIDUAL EXPONENTIAL TERMS			
m	Case 4	Case 5	Case 6
0	0.9999999	0.9999990	0.9999901
1	0.1111110	0.1111101	0.1111012
2	0.0399999	0.0399990	0.0399901
3	0.0204081	0.0204072	0.0203983
4	0.0123456	0.0123447	0.0123358
5	0.0082644	0.0082635	0.0082546
6	0.0059171	0.0059162	0.0059073
7	0.0044443	0.0044435	0.0044346
8	0.0034601	0.0034592	0.0034504
9	0.0027700	0.0027691	0.0027602
10	0.0022675	0.0022666	0.0022577
20	0.0005948	0.0005939	0.0005851
30	0.0002686	0.0002678	0.0002591
40	0.0001523	0.0001514	0.0001429
50	0.0000979	0.0000970	0.0000886
100	0.0000247	0.0000238	0.0000166
150	0.0000109	0.0000101	0.0000045
200	0.0000061	0.0000053	0.0000013
250	0.0000039	0.0000031	0.0000003
300	0.0000027	0.0000019	0.0000001
315	0.0000024	0.0000017	0.0000000
350	0.0000019	0.0000013	
400	0.0000015	0.0000008	
450	0.0000011	0.0000006	
500	0.0000009	0.0000004	
550	0.0000007	0.0000002	
600	0.0000006	0.0000002	
650	0.0000005	0.0000001	
700	0.0000004	0.0000001	
746	0.0000004	0.0000000	
750	0.0000004		
800	0.0000003		
850	0.0000003		
900	0.0000002		
950	0.0000002		
1000	0.0000002		

	Case 7	Case 8	Case 9
Datf/L ²	1.0E-05	1.0E-04	1.0E-03
SUM	1.225	1.206	1.146
1-8*SUM/Pi ²	0.007	0.023	0.071
Log(G/wAom)	-2.2	-1.64	-1.15
Log(Datf/L ²)	-5	-4	-3

INDIVIDUAL EXPONENTIAL TERMS			
m			
0	0.9999013	0.9990135	0.9901789
1	0.1110125	0.1101285	0.1016672
2	0.0399014	0.0390251	0.0312537
3	0.0203097	0.0194447	0.0125827
4	0.0122474	0.0113971	0.0055504
5	0.0081664	0.0073342	0.0025036
6	0.0058193	0.0050081	0.0011162
7	0.0043468	0.0035594	0.0004824
8	0.0033629	0.0026015	0.0001997
9	0.0026731	0.0019398	0.0000785
10	0.0021710	0.0014674	0.0000292
15	0.0009464	0.0004031	0.0000001
16	0.0008247	0.0003135	0.0000000
20	0.0005039	0.0001132	0.0000000
30	0.0001861	0.0000068	0.0000000
40	0.0000798	0.0000002	0.0000000
44	0.0000578	0.0000001	0.0000000
45	0.0000533	0.0000000	0.0000000
50	0.0000358	0.0000000	0.0000000
60	0.0000161		
70	0.0000071		
80	0.0000030		
90	0.0000012		
100	0.0000005		
110	0.0000002		
120	0.0000001		
121	0.0000000		

	Case 10	Case 11	Case 12
DAtf/L ²	1.0E-02	1.00E-01	1.00E+00
SUM	0.955	0.373	0.000
1-8*SUM/Pi ²	0.226	0.698	1.000
Log(G/wAom)	-0.647	-0.156	0.000
Log(DAtf/L ²)	-2	-1	0

m	INDIVIDUAL EXPONENTIAL TERMS		
0	0.9060	0.3727	0.0001
1	0.0457	0.0000	0.0000
2	0.0034		
3	0.0002		
4	0.0000		